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On Organic Compounds of Arsenic. Part IV. Reaction between the Grignard Reagent and Arsenic Trisulphide.

By

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ABSTRACT

The actions of arsenic trisulphide on phenylmagnesium bromide, α-naphthylmagnesium bromide and p-tolylmagnesium bromide were studied. An interesting fact observed is that arsenic trisulphide acts upon p-tolylmagnesium bromide in two different ways according to the mode of the preparation. When arsenic trisulphide precipitated by hydrogen sulphide in an acid solution and subsequently dried at 100° was used, tri-p-tolylarsine sulphide and di-p-tolylarsine sulphide were produced with a small quantity of tri-p-tolylarsine, while arsenic trisulphide precipitated by hydrogen sulphide and subsequently treated with carbon dioxide to drive off the excess of hydrogen sulphide, washed with carbon bisulphide and then dried at 100°, gave tri-p-tolylarsine and di-p-tolylarsine sulphide but not tri-p-tolylarsine sulphide.

Di-α-naphthylarsine sulphide was obtained in the form of colourless crystals, m. p. 185–186°. It was also prepared from di-α-naphthylarsine oxide or di-α-naphthylchloroarsine by the action of hydrogen sulphide, and was transformed to di-α-naphthylarsinic acid by treating it with chlorine. $2[(C_{10}H_7)_2As]_2S+7\,Cl_2=4(C_{10}H_7)_2AsCl_3+S_2Cl_2$, $(C_{10}H_7)_2AsCl_3+2H_2O=(C_{10}H_7)_2AsO_2H+3HCl$. The formation of sulphur monochloride in this reaction was easily recognized by its characteristic smell.

Triphenylarsine sulphide mercurichloride, $(C_6H_5)_3AsS.HgCl_2$, m. p. 239–241°, tri-p-tolylarsine sulphide mercurichloride, $(C_7H_7)_3AsS.HgCl_2$, m. p. 227–229°, were prepared and their properties were recorded.

From the study of the action of arsenic trisulphide on the Grignard reagent the interesting fact was found that the mode of its preparation has a great influence upon the reaction. Finely powdered arsenic trisulphide and phenylmagnesium bromide reacted energetically and gave triphenylarsine sulphide and triphenylarsine when the reaction product was treated with water and dilute acetic acid. Diphenylarsine sulphide, which is rather

difficult to crystallize, was identified by transforming it into diphenylarsinic acid. The reaction between p-tolylmagnesium bromide and arsenic trisulphide smoothly set in and produced tri-p-tolylarsine sulphide with an oily product, which could easily be oxidized into di-p-tolylarsinic acid. By the reaction between *α*-naphthylmagnesium bromide and arsenic trisulphide, di-*α*-naphthylarsine sulphide was only produced.

From the above experiments, it will be noticed that arsenic trisulphide reacts upon the Grignard reagent just in a way analogous to the action of the trioxide[1] and produces the secondary and tertiary arsine compounds, but not the primary thus:

$$As_2S_3 + 4RMgBr = (R_2As)_2S + 2MgS + 2MgBr_2, \qquad (i)$$

$$(R_2As)_2S + 2RMgBr = 2R_3As + MgS + MgBr_2. \qquad (ii)$$

In the case of *α*-naphthylmagnesium bromide, the reaction comes to a stop at the stage of equation (i), probably because *α*-naphthylmagnesium bromide does not react on di-*α*-naphthylarsine sulphide so as to change the latter into the tertiary compound. To confirm whether the reaction (ii) actually takes place, diphenylarsine sulphide prepared by treating the corresponding arsine oxide with hydrogen sulphide, was treated with phenylmagnesium bromide. As was expected, triphenylarsine was obtained as the only reaction product, triphenylarsine sulphide not being produced.

The formation of diarylarsinic acid by oxidation of diarylarsine sulphide was confirmed by experiment as was described in the experimental part of this memoir.

The reaction may be represented by the following equations.

$$2[(C_{10}H_7)_2As]_2S + 7Cl_2 = 4(C_{10}H_7)_2AsCl_3 + S_2Cl_2,$$

$$(C_{10}H_7)_2AsCl_3 + 2H_2O = (C_{10}H_7)_2AsO_2H + 3HCl.$$

As to the formation of triphenylarsine sulphide and tri-p-tolylarsine sulphide a doubt naturally arises that they may be the products of reactions of triarylarsines upon sulphur which may have existed as an impurity in the arsenic trisulphide, for those tertiary arsines are generally very active towards sulphur and combine with it without difficulty[2].

To make this ambiguous point clear several experiments were performed arsenic trisulphide prepared in four diffrent ways being used.

I. The precipitates formed in a warm hydrochloric acid solution by hydrogen sulphide were well washed with hot water containing a small quantity of hydrogen sulphide and dried in a desiccator and then at 100° in an air bath.

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1 K. Matsumiya and M. Nakai, These Memoirs, **8**, 307 (1925).

2 La Coste and Michælis, Lieb. Ann., **201**, 244 (1880); Michælis, Lieb. Ann., **321**, 204 (1902).

II. After the precipitates were dried as above, they were washed in a Soxlet tube with carbon bisulphide and then dried at 100°.

III. The precipitates together with the mother liquor were treated with carbon dioxide gas so as to expel hydrogen sulphide completely. Then they were well washed with warm water containing a small quantity of hydrogen sulphide, dried in a desiccator and finally heated at 100° in an air bath.

IV. The precipitates prepared in the manner described in III were washed with carbon bisulphide in a Soxlet tube and dried in an air bath at 100°.

All these arsenic trisulphides readily acted upon p-tolylmagnesium bromide, but the reaction products differed in each case.

Sulphide (I) The main product was tri-p-tolylarsine sulphide, together with a small quantity of tri-p-tolylarsine and di-p-tolylarsine sulphide.

Sulphide (II) Tri-p-tolylarsine was chiefly produced. A small quantity of tri-p-tolylarsine sulphide and di-p-tolylarsine sulphide was also produced.

Sulphide (III) and (IV) Tri-p-tolylarsine and di-p-tolylarsine sulphide were formed, but no tri-p-tolylarsine sulphide.

According to the investigation of O. Puller,[1] arsenic trisulphide prepared by method (I) contains about 2 % more sulphur than the theory demands, and the above experiment shows that the more free sulphur is washed away the less tri-p-tolylarsine sulphide is formed. These facts seem at first sight to show that the formation of tri-p-tolylarsine sulphide is due to the action of sulphur. Nevertheless, the quantity of tri-p-tolylarsine sulphide produced was rather great to be regarded as having been formed by the action of sulphur contained as an impurity. No such different reactions with arsenic trisulphide could be observed in the case of phenylmagnesium bromide, triphenylarsinesulphide being found almost in the same quantity in every case. Accordingly the presence of sulphur as an imprity was seen to have no influence upon the resulting product.

EXPERIMENTAL PART.

1. Action of Phenylmagnesium Bromide upon Arsenic Trisulphide.

To the Grignard reagent prepared from 15·7 grm. (1/10 mol.) of bromobenzene, 2·5 grm. (1/10 mol.) of magnesium and a trace of methyl

1 Z. Anal. Chem., **10**, 41 (1871).

iodide in 30 c.c of dry ether, 6·2 grm. (1/40 mol.) of powdered arsenic trisulphide were gradually added. A vigorous reaction took place accompanied by heat generation. When the reaction subsided, the reaction product was boiled for an hour in a water-bath. After standing over night, the product was decomposed with water and then with dilute acetic acid and distilled with steam to drive off ether and diphenyl. The residue was extracted with ether and the ethereal solution was dried with anhydrous sodium sulphate and evaporated when a residue solidifying gradually on standing was obtained. It was washed with ether to remove a yellow oily substance adhering and recrystallized from alcohol. Colourless needles melting at 161–162°[1] were obtained. The yield was 2·3 grm. The analyses for arsenic and sulphur gave the following values.

0·2521 grm. of the sample gave 0·1716 grm. $BaSO_4$.

0·2487 grm. substance required 29·4 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_3AsS$	Found
As	22·17	22·16
S	9·45	9·35

The ethereal washing was concentrated and kept in vacuo for many days, and the crystals thus separated were pressed between filter-papers to remove a yellow oily substance and recrystallized from ether. About 2·2 grm. of colourless crystals melting at 58–60° were obtained. They were analysed with the following result: –

0·1368 grm. substance required 17·82 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_3As$	Found
As	24·49	24·42

The yellow oily substance absorbed in filter-papers was extracted with ether and treated with an ethereal solution of mercuric chloride when white crystalline precipitates were instantly formed. The precipitates were dissolved in boiling alcohol and into the solution hydrogen sulphide was passed. The filtered solution, on concentration, gave fine needles which were washed with a small quantity of ether and recrystallized from alcohol. The colourless needles (yield, 0·2 grm,) thus formed melted at 161–162°. They were identified as triphenylarsine sulphide.

On evaporating the ethereal washing, an oily residue solidifying gradually on standing was left. After removal of yellow oily impurities, the residue was recrystallized from ether several times, and colourless crystals melting at 58–60° were finally obtained. The yield was 0·7 grm. They

1 Philips, Ber. D. Chem. Ges., **19**, 1032 (1886); La Coste and Michælis, loc. cit

were proved to be triphenylarsine on their properties being examined.

The ethereal solution containing mercuric chloride was repeatedly washed with dilute hydrochloric acid and then saturated with chlorine. After the evaporation of ether, the residue was treated with a dilute caustic soda solution and decolourized with animal charcoal. On acidifying the solution with hydrochloric acid, white precipitates were produced. When recrystallized from hot water 0·5 grm. of colourless crystals melting at 170–171°[1] was obtained. Its analytical result was as follows:–

0·1415 grm. substance required 21·53 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_2AsO.OH$	Found
As	28·61	28·53

In the above reactions, all sorts of arsenic trisulphide were seen to give nearly the same result.

2. *Action of p-Tolylmagnesium Bromide upon Arsenic Trisulphide*[2].

a) The trisulphide prerared by method (I) was used.

The ethereal solution of p-tolylmagnesium bromide prepared from 9 grm. (1/20 mol.) of p-bromotoluene, 1·3 grm. (1/20 mol.) of magnesium and a trace of methyl iodide in 30 c.c of dry ether was treated slowly with 3·1 grm. (1/80 mol.) of arsenic trisulphide, and then the mixture was boiled for an hour in a water-bath. The product was decomposed with water and dilute acetic acid and subjected to steam distillation to remove ether and di-p-tolyl. The residue was extracted with ether and the ethereal solution was dried with sodium sulphate. After removal of ether, a viscid oil crystallizing on standing was obtained. The solidified mass was pressed between filter-papers to remove a yellowish oily substance and washed with a small quantity of alcohol. By several fractional crystallizations from alcohol, 0·8 grm. of colourless fine needles melting at 166–167°[3] and 0·2 grm. of colourless rhombic crystals melting at 146–147°[4] were isolated. The analyses gave the following results.

0·1623 grm. of the needle crystals required 17·1 c.c of N/20 iodine solution.

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1 K. Matsumiya and M. Nakai, loc. cit., 311; La Coste and Michælis, loc. cit., 231,

2 In these experiments, we used four specimens of arsenic trisulphide prepared by different methods as described before..

3 Michælis, loc. cit.

4 K. Matsumiya and M. Nakai, loc. cit., 312; La Coste, Lieb. Ann., **208**, 26 (1881); Michælis, loc. cit., 200.

0·2511 grm. substance gave 0·1550 grm. $BaSO_4$.

	Calc. for $(CH_3 . C_6H_4)_3AsS$	Found
As	19·72	19·75
S	8·43	8·47

0·1443 grm. of the rhombic crystals required 16·55 c.c of N/20 iodine solution.

	Calc. for $(CH_3 . C_6H_4)_3As$	Found
As	21·53	21·50

The oily substance was dissolved in ether and treated with an ethereal solution of mercuric chloride. The mercurichloride then formed was dissolved in boiling alcohol and then saturated with hydrogen sulphide to remove mercury as mercuric sulphide. On concentration, the filtered alcoholic solution gave 0·2 grm. of needle crystals together with a small quantity of rhombic crystals.

The ethereal solution containing the excess of mercuric chloride was well washed with dilute hydrochloric acid and treated with chlorine. Then it was extracted with a dilute caustic soda solution and decolourized with animal charcoal; on acidifying it with hydrochloric acid, colourless crystals crystallizing in fine needles from hot water were obtained. It melted at 173–174°[1]. The yield was 0·4 grm. The analytical result was as follows:–

0·1418 grm. substance required 19·25 c.c of N/20 iodine solution.

	Calc. for $(CH_3 . C_6H_4)_2AsO . OH$	Found
As	25·84	25·46

b) The trisulphide prepared by method (II) was used.

Experiments were carried out under the same conditions as above, and as main products, 1·2 grm. of tertiary arsine and 0·2 grm. of tertiary arsine sulphide were obtained. From the mercurichloride 0·2 grm. of tertiary arsine accompanied by a small amount of tertiary arsine sulphide was obtained, and from the oily substance, 0·1 grm. of secondary arsinic acid.

c) The trisulphide prepared by method (III) or (IV) was used.

As the products, 2·2 grm. of tertiary arsine, 0·2 grm. of the same arsine from its mercurichloride and 0·1 grm. of secondary arsinic acid from the oily substance were obtained. Tertiary arsine sulphide was never produced in this case.

3. Action of α-Naphthylmagnesium Bromide upon Arsenic Trisulphide.

To the ethereal solution of α-naphthylmagnesium bromide prepared

1 K. Matsumiya and M. Nakai, loc. cit.; La Coste, loc. cit., 20.

from 20·7 grm. (1/10 mol.) of *α*-bromonaphthalene, 2·5 grm. (1/10 mol.) of magnesium and a piece of iodine in 60 c.c of dry ether, 6·2 grm. (1/40 mol.) of arsenic trisulphide were added little by little and then the mixture was boiled for an hour on a water-bath. It was decomposed with water and dilute acetic acid and subjected to steam distillation to remove ether and naphthalene. The residue was extracted with chloroform, and on concentrating this chloroform solution a yellowish solid was obtained. It was extracted with ether in a Soxlet tube to remove coloured impurities when a pale yellow powder was left in the apparatus. It was recrystallized several times from chloroform, and colourless crystals were obtained whose melting point was 185–186°. The yield was 7·2 grm. It was analyzed and gave the following results: –

0·1640 grm. substance gave 0·4184 grm. CO_2 and 0·0630 grm. H_2O.
0·1608 grm. substance required 18·55 c.c of N/20 iodine solution.
0·5670 grm. substance gave 0·1866 grm. $BaSO_4$.

	Calc. for $[(C_{10}H_7)_2As]_2S$	Found
As	21·72	21·64
C	69·54	69·58
H	3·99	4·30
S	4·64	4·52

Di-*α*-naphthylarsine sulphide is insoluble in ether and alcohol, soluble in benzene and more easily so in hot benzene, carbon bisulphide and chloroform.

4. *Action of Phenylmagnesium Bromide upon Diphenylarsine Sulphide.*

The Grignard reagent prepared from 4 grm. (1/40 mol.) of bromobenzene, 0·7 grm. (1/40 mol.) of magnesium and a trace of methyl iodide in 30 c.c of dry ether was treated with 2·5 grm. (1/200 mol.) of diphenylarsine sulphide, and then the mixture was boiled for five hours on a water-bath. On cooling, the reaction product was decomposed with water and dilute acetic acid, and ether and diphenyl were distilled off with steam. The residue was extracted with ether and the extract was dried with sodium sulphate. On concentrating the solution, a yellow viscid oil was obtained which solidified on standing. The crystals were separated from oily matter by pressing between filter-papers and recrystallized from ether repeatedly. 1·8 grm. of colourless crystals melting at 58–60° were obtained. They were analyzed with the following result.

0·1515 grm. substance required 19·85 c.c of N/20 iodine solution.

	Calc. for $(C_6H_5)_3As$	Found
As	24·49	24·57

The oily matter was dissolved in ether and treated with an ethereal solution of mercuric chloride, whereby white precipitates were instantly formed. From this mercurichloride, 0·5 grm. of triphenylarsine was obtained by treating it with alcoholic potash. No triphenylarsine sulphide was obtained.

5. Formation of Triphenylarsine Sulphide Mercurichloride.

On adding the ethereal solution of mercuric chloride to triphenylarsine sulphide in an alcoholic medium, a white crystalline powder was instantly precipitated. It was recrystallized from hot absolute alcohol, and colourless crystals melting at 239–241° were obtained.

Mercury was estimated as follows: – The substance was dissolved in hot absolute alcohol and then saturated with hydrogen sulphide. The black mercuric sulphide produced was collected in a Gooch crucible, washed with alcohol and water, dried at 105° and weighed. By this method 0.1677 grm. of the sample gave 0·0638 grm. HgS.

	Calc. for $(C_6H_5)_3AsS \cdot HgCl_2$	Found
Hg	32·91	32·80

Triphenylarsine sulphide mercurichloride is soluble in hot absolute alcohol, less so in dilute spirit and insoluble in ether and water. It was unaffected by cold aqueous caustic potash, but when heated it gave triphenylarsine sulphide liberating mercury as mercuric oxide according to the following equation.

$$(C_6H_5)_3AsS \cdot HgCl_2 + 2KOH = (C_6H_5)_3AsS + HgO + 2KCl + H_2O.$$

When treated with cold alcoholic potash, it also yielded triphenylarsine sulphide. It was also decomposed by hydrogen sulphide in hot alcoholic solution, and gave triphenylarsine sulphide.

6. Formation of Tri-p-tolylarsine Sulphide Mercurichloride.

The ethereal solution of mercuric chloride was added to tri-p-tolylarsine sulphide in the same medium, whereby white crystalline powder was produced. After several recrystallizations from hot alcohol colourless crystals melting at 227–229° were obtained. Analysis gave the following result: – 0·1409 grm. substance gave 0·0501 grm. HgS.

	Calc. for $(C_7H_7)_3AsS \cdot HgCl_2$	Found
Hg	30·77	30·66

Tri-p-tolylarsine sulphide mercurichloride is easily soluble in hot absolute alcohol and insoluble in ether and water. On heating with aqueous caustic

potash or treating with cold alcoholic potash or with hydrogen sulphide in an alcoholic medium it gave tri-p-tolylarsine sulphide.

7. Action of Hydrogen Sulphide upon Di-α-naphthylarsine Oxide.

Carbon bisulphide solution of di-α-naphthylarsine oxide was saturated with hydrogen sulphide and after removal of the solvent the residue was extracted with ether in a Soxlet tube. A slightly yellow coloured powder was left behind which, when recrystallized from chloroform, formed colourless crystals melting at 185–186°. Its analytical result for arsenic was as follows:–

0·1552 grm. substance required 17·82 c.c of N/20 iodine solution.

	Calc. fot $[(C_{10}H_7)_2As]_2S$	Found
As	21·72	21·53

8. Action of Hydrogen Sulphide upon Di-α-naphthylchloroarsine.

Dry hydrogen sulphide was passed into a benzene-alcoholic solution of di-α-naphthylchloroarsine. On evaporating the solvent a brownish residue was obtained which was then washed with ether in a Soxlet apparatus. After several recrystallizations from chloroform it was transformed into crystals melting at 185–186°.

0·1537 grm. substance required 17·7 c.c of N/20 iodine solution.

	Calc. for $[(C_{10}H_7)_2As]_2S$	Found
As	21·72	21·59

9. Action of Chlorine upon Di-α-naphthylarsine Sulphide.

Dry ether in which di-α-naphthylarsine sulphide was suspended was saturated with dry chlorine, whereby yellow precipitates were instantly formed. Ether was decanted off and the precipitates were washed well with absolute ether to remove the sulphur monochloride formed, and dried by passing dry air over it. It was analyzed after having been kept in vacuo over sulphuric acid.

0·1587 grm. of the sample required 14·45 c.c of N/20 iodine solution.

0·1508 grm. substance gave 0·1454 grm. AgCl.

	Calc. for $(C_{10}H_7)_2AsCl_3$	Found
As	17·22	17·07
Cl	24·43	23·86

Thus di-α-naphthylarsine sulphide was converted into di-α-naphthylarsine trichloride[1] and sulphur monochloride, the latter of which was recognized

1 K. Matsumiya and M. Nakai, loc. cit., 316.

by its characteristic odour.

10. Direct Formation of Di-α-naphthylarsinic Acid from Di-α-naphthylarsine Sulphide

A mixture of ether and water in which di-α-naphthylarsine sulphide was suspended was saturated with chlorine. The reaction product was treated with a dilute caustic soda solution and decolourized with animal charcoal. On acidifying the solution with hydrochloric acid, white precipitates were obtained which after several recrystallizations from benzene-ether solution formed a white amorphous powder melting at 228-229°.[1] Analysis gave the following value for arsenic.

0·1334 grm. substance required 14·72 c.c of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_2AsO.OH$	Found
As	20·70	20·68

1 K. Matsumiya and M. Nakai, loc. cit.

On Carbolthionic Acids and their Esters. Part. II.

By

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ABSTRACT.

As the results of experiments further continued on the synthesis of thionic esters and acids the following compounds were isolated and their properties were examined:

Thionacetic esters:—Methylester, n-Propylester, Isopropylester, Butylester, Isobutylester, Benzylester, m-Tolylester, p-Tolylester, Naphthylester.

Thionpropionic ester:—n-Propylester, Isopropylester, Butylester, Isobutylester, Phenylester, Benzylester.

Thionbenzoic ester:—Methylester, Propylester, Isopropylester, Butylester, Isobutylester, Isoamylester, Phenylester, Benzylester, β-Naphthylester.

Thionphenylacetic ester:—Methylester, Propylester, Isopropylester, Butylester, Isobutylester, Isoamylester, Phenylester, Benzylester.

Thionparatoluic ester:—Methylester, Propylester, Isopropylester, Butylester, Isobutylester, Isoamylester, Benzylester.

Thionoxalic ester:—Dimethylester, Diethylester, Di-isopropylester.

Acids:—Thionacetic acid, Thionpropionic acid, Thionphenylacetic acid, Thionparatoluic acid, Thion-β-naphtoic acid, Thionoxalic acid.

After the first communication[1] had been published many new thionic esters were successively prepared according to the method of M. Matsui, and as these esters were found to saponify smoothly by the action of alcoholic potash it became now possible to isolate free thionic acids in a purer state.

The present communication gives an account of these esters and acids as so far obtained.

I Thionacetic Esters.

1. Methylester CH_3CSOCH_3

This was prepared from acetiminomethylester by treating its ethereal

1 These Memoirs, **9**, 237 (1926).

solution with dry hydrogen sulphide. It is a light-greenish-yellow-coloured liquid with a disagreeable odour. The portion distilling at 88-91° was collected and analysed.

0·0741 grm. substance gave 0·2034 grm. Ag_2S

	Calc.	Found.	
S	35·57	35·51	%

The following physical constants were determined:

Sp. Gr. $d\left(\frac{28°}{4}\right) = 0.9002$, Index of refraction $n = 1·4212$ (28°).

It fumes in a moist atmosphere, especially in the presence of alcoholic vapour.

2. n-Propylester $CH_3CSOC_3H_7$

This is also a liquid of a pale yellow colour fuming in a moist atmosphere. The portion boiling at 125-130° was examined and analysed.

$d\left(\frac{28°}{4}\right) = 0\,8952$, $n = 1·4283$ (28°), viscosity = 0·7823 (28°).

0·1217 grm. substance gave 0·2556 grm. Ag_2S

	Calc.	Found.	
S	27·13	27·17	%

3. Isopropylester $CH_3CSOC_3H_7$

A slightly yellow-coloured liquid boiling at 119°-122° and having the following physical constants.

$d\left(\frac{22°}{4}\right) = 6·8901$, $n = 1·4501$ (22°), viscosity = 0·7052 (22°)

Analysis: 0·1001 grm. substance gave 0·2104 grm. Ag_2S

	Calc.	Found.	
S	27·13	27·19	%

4. Butylester $CH_3CSOC_4H_9$

This ester differs from methyl or propylester in not fuming in a moist atmosphere. The portion having a boiling point of 146°-149° was used for the determination of the physical constants and for analysis.

$d\left(\frac{29°}{4}\right) = 0·8883$, $n = 1\,4196$ (28°), viscosity = 0·8492 (29°).

0·1482 grm. of the ester gave 0·2720 grm. Ag_2S

	Calc.	Found.	
S	24·25	23·76	%

5. Isobutylester $CH_3CSOC_4H_9$

This ester boils at 135°-140° and shows the following physical properties.

$d\left(\frac{26°}{4}\right) = 0·8875$, $n = 1·4316$ (26°) viscosity = 0·8903 (26°)

Analysis: 0·1058 grm. substance gave 0·1985 grm. Ag_2S.

	Calc.	Found.	
S	24·25	24·27	%

6. Benzylester $CH_3CSOCH_2C_6H_5$

This is a yellow liquid boiling at 115°-120° under 27-29 mm. pressure.

$d\left(\frac{25°}{4}\right) = 1·0296$, $n = 1·5492$ (26°) viscosity = 2·1711 (25°).

Analysis: 0·1247, grm. substance gave 0·1856 grm. Ag_2S.

	Calc.	Found.	
S	19·29	19·25	%

7. Tolylester $CH_3CSOC_6H_4CH_3$

Meta-and paratolyl esters were obtained both as yellow liquids, the former of which boils at 110°-112° and the latter at 109°-110° under 25-26 mm. pressure.

8. β-Naphthylester $CH_3CSOC_{10}H_7$

This was obtained as a yellow crystalline substance. Its properties, however, could not be examined because of the lack of material.

II. Thionpropionic Esters.

1. Propylester $C_2H_5CSOC_3H_7$

This is a pale yellow liquid which fumes in a moist atmosphere. The portion boiling at 139°-144° was examined and analysed.

$d\left(\frac{28°}{4}\right) = 0\,8835$, $n = 1·4396$ (28°) viscosity = 0·8256 (28°).

0·1564 grm. ester gave 0·2894 grm. Ag_2S.

	Calc.	Found.	
S	24·25	23·94	%

2. Isopropylester $C_2H_5CSOC_3H_7$

A pale-yellow liquid boiling at 137°-140°, $d\left(\frac{22°}{4}\right) = 0·8714$, $n = 1·4372$ (25°), viscosity = 0·7318 (22°)

Analysis: 0 1408 grm. substance gave 0·2638 grm. Ag_2S.

	Calc.	Found.	
S	24·25	24·24	%

3. Butylester $C_2H_5CSOC_4H_9$

A yellow liquid boiling at 164°-167°, $d\left(\frac{28°}{4}\right) = 0·8618$, $n = 1·4303$ (28°), viscosity = 0·8799 (28°).

Analysis: 0·1933 grm. substance gave 0·3279 grm. Ag_2S.

	Calc.	Found.	
S	21·93	21·95	%

4. Isobutylester $C_2H_5CSOC_4H_9$

A yellow liquid, B.P. = 153°-157°. $d\left(\frac{25°}{4}\right)$ = 0·8678, n = 1·4286 (26°), viscosity = 0·9001 (25°)

Sulphur was determined with the following results:

0·0878 grm. substance gave 0·1476 grm. Ag_2S

	Calc.	Found.	
S	21·93	21·75	%

5. Benzylester $C_2H_5CSOCH_2C_6H_5$

A yellow liquid boiling at 132°-136° under 28-30 mm. pressure.

$d\left(\frac{26°}{4}\right)$ 1·0009, n = 1·5178 (26°), viscosity = 2·0846 (26°)

Analysis: 0·1054 grm. substance gave 0·1447 grm. Ag_2S

	Calc.	Found.	
S	17·79	17·76	%

Phenylester was also isolated as a yellow liquid.

III. Thionbenzoic Esters.

1. Methylester $C_6H_5CSOCH_3$

This is an intensely yellow-coloured liquid having a disagreeable odour, and distils at 112°-115° under 26 mm. pressure.

$d\left(\frac{28°}{4}\right)$ = 1·0710, n = 1·5606 (29°), viscosity = 1·6866 (28°)

Analysis: 0·1221 grm. substance gave 0·1976 grm. Ag_2S.

	Calc.	Found.	
S	21·07	20·94	%

2. Propylester $C_6H_5CSOC_3H_7$

An intensely yellow-coloured liquid boiling at 127°-132° under 29 mm. pressure.

$d\left(\frac{28°}{4}\right)$ = 1·0133, n = 1·5289 (28°), viscosity = 2·4550 (28°).

Analysis: 0·1446 grm. substance gave 0·1942 grm. Ag_2S.

	Calc.	Found.	
S	17·79	17·37	%

3. Isopropylester $C_6H_5CSOC_3H_7$

A liquid of deep yellow colour. B.P. = 117°-122° under 27 mm. presure, $d\left(\frac{27°}{4}\right)$ = 1·0060, n = 1·5241 (27°), viscosity = 2·1376 (27°).

Analysis: 0 1048 grm. substance gave 0 1418 grm. Ag_2S.

	Calc.	Found.	
S	17·79	17·50	%

4. Butylester $C_6H_5CSOC_4H_9$

An intensely yellow-coloured liquid boiling at 137°-142° under 23 mm. presuure. $d\left(\frac{28^\circ}{4}\right) = 0\ 9732$, $n = 1{\cdot}5293(28^\circ)$, viscosity $= 2\ 6357(28^\circ)$

Analysis: 0·1102 grm. substance gave 0·1416 grm. Ag_2S

	Calc.	Found.	
S	16·51	16·62	%

5. Isobutylester $C_6H_5CSOC_4H_9$

This ester boils at 133°-137° under 27 mm. pressure. $d\left(\frac{28^\circ}{4}\right) = 0{\cdot}9694$, $n = 1{\cdot}5049\ (27^\circ)$, viscosity $= 2{\cdot}5415\ (28^\circ)$.

Analysis: 0·1072 grm. substance gave 0·1328 grm. Ag_2S.

	Calc.	Found.	
S	16·51	16·03	%

6. Isoamylester $C_6H_5CSOC_5H_{11}$

A liquid of an intense yellow colour boiling at 170°-175° under 54 mm. pressure. $d\left(\frac{23^\circ}{4}\right) = 0{\cdot}9748$, $n = 1{\cdot}4974\ (25^\circ)$, viscosity $= 3{\cdot}1700\ (23^\circ)$.

Analysis: 0·1031 grm. substance gave 0·1224 grm. Ag_2S.

	Calc.	Found.	
S	15·39	15·36	%

7. Phenylester $C_6H_5CSOC_6H_5$

This was obtained as a yellow solid which boils at 155°-160° under 40 mm. pressure.

8. Benzylester $C_6H_5CSOCH_2C_6H_5$

A yellow viscous liquid boiling at 165°-170° under 38-40 mm. pressure.

Analysis: 0·1804 grm. substance gave 0 1964 grm. Ag_2S.

	Calc.	Found.	
S	14·05	14·08	%

9. β-Naphthylester $C_6H_5CSOC_{10}H_7$

Though this was isolated as an intensely yellow-coloured solid its physical properties were not determined.

IV Thionphenylacetic Esters.

1. Methylester $C_6H_5CH_2CSOCH_3$

This was prepared from phenylacetiminomethylester by the method

of M. Matsui as a yellow liquid boiling at 145°-149° under 82-84 mm. pressure.

$d\left(\frac{28^\circ}{4}\right) = 1.0551$, $n = 1.5612\ (30^\circ)$, viscosity $= 1.9296\ (28^\circ)$.

Analysis: 0.1082 grm. substance gave 0.1591 grm. Ag_2S

	Calc.	Found.	
S	19.29	19.02	%

2. Propylester $C_6H_5CH_2CSOC_3H_7$

This is a yellow liquid boiling at 130°-133° under 25 mm. pressure, and shows the following physical properties.

$d\left(\frac{27^\circ}{4}\right)$ 1.0139, $n = 1.5104\ (29^\circ)$, viscosity $= 2.7187\ (27^\circ)$.

Analysis: 0.1372 grm. substance gave 0.1732 grm. Ag_2S

	Calc.	Found.	
S	16.51	16.33	%

3. Isopropylester $C_6H_5CH_2CSOC_3H_7$

This is also a yellow liquid which boils at 140°-145° under 50 mm. pressure. $d\left(\frac{22^\circ}{4}\right)$ 1.0078, $n = 1.5026\ (25^\circ)$, viscosity $= 2.4672\ (22^\circ)$.

Analysis: 0.1733 grm. substance gave 0.2210 grm. Ag_2S

	Calc.	Found.	
S	16.51	16.50	%

4. Butylester $C_6H_5CH_2CSOC_4H_9$

A yellow liquid boiling at 155°-160° under 36 mm. pressure.

$d\left(\frac{28^\circ}{4}\right) = 0.9930$, $n = 1.5138\ (28^\circ)$, viscosity $= 2.9127\ (28^\circ)$.

Analysis: 0.1282 grm. substance gave 0.1552 grm. Ag_2S.

	Calc.	Found.
S	15.39	15.66

5. Isobutylester $C_6H_5CH_2CSOC_4H_9$

A yellow liquid which boils at 138°-143° under 25 mm. pressure.

$d\left(\frac{28^\circ}{4}\right) = 1.0010$, $n = 1.5065\ (28^\circ)$, viscosity $= 2.7713\ (28^\circ)$.

Analysis: 0.1001 grm. substance gave 0.1130 grm. Ag_2S.

	Calc.	Found.	
S	15.39	14.60	%

6. Isoamylester $C_6H_5CH_2CSOC_5H_{11}$

A yellow liquid, B.P. = 168°-169° under 50 mm. pressure,

$d\left(\frac{23^\circ}{4}\right) = 0.9801$, $n = 1.4902\ (25^\circ)$, viscosity $= 3.1369\ (23^\circ)$.

Analysis: 0·1556 grm. substance gave 0·1730 grm. Ag_2S

	Calc.	Found.	
S	14·42	14·38	%

7. Phenylester $C_6H_5CH_2CSOC_6H_5$

This was obtained as a yellow viscous liquid boiling at 202°-206° under 65 mm. pressure.

8. Benzylester $C_6H_5CH_2CSOCH_2C_6H_5$

A yellow liquid whose boiling point under 26 mm. pressure was found to be 180°-185°.

$d\left(\frac{26^\circ}{4}\right) = 1·0866$, viscosity = 5·2005 (26°).

Analysis: 0·1322 grm. substance gave 0·1362 grm. Ag_2S

	Calc.	Found.	
S	13·23	13·33	%

V Thionparatoluic Esters.

1. Methylester $C_7H_7CSOCH_3$

This was prepared from paratoluiminomethylester according to M. Matsui's general mode of formation of thionic esters.

An intensely yellow-coloured liquid boiling at 170°-173° under 150 mm. pressure. $d\left(\frac{26^\circ}{4}\right) = 1·0478$, viscosity = 2·5396 (26°).

Analysis: 0·1368 grm. substance gave 0·2059 grm. Ag_2S.

	Calc.	Found.	
S	19·29	19·47	%

2. Propylester $C_7H_7CSOC_3H_7$

A yellow liquid boiling at 130°-135° under 23 mm. pressure.

$d\left(\frac{26^\circ}{4}\right) = 0·9858$, n = 1·5289 (23°). viscosity = 2·1789 (26°).

Analysis: 0·1504 grm. substance gave 0·1882 grm. Ag_2S.

	Calc.	Found.	
S	16·51	16·19	%

3. Isopropylester $C_7H_7CSOC_3H_7$

A yellow liquid, B.P. = 138°-142° under 48-50 mm. pressure.

$d\left(\frac{22^\circ}{4}\right) = 0·9880$, viscosity = 1·9882 (22°).

4. Butylester $C_7H_7CSOC_4H_9$

A liquid of a deep yellow colour boiling at 150°-152° under 23 mm. pressure. $d\left(\frac{22^\circ}{4}\right) = 0·9905$, n = 1·5315 (23°), viscosity = 2·7505 (22°).

Analysis: 0·1858 grm. substance gave 0·2115 grm. Ag_2S

	Calc.	Found	
S	15·39	14·73	%

5. Isobutylester $C_7H_7CSOC_4H_9$

An intensely yellow-coloured liquid boiling at 144°-148° under 38-40 mm. pressure. $d\left(\frac{25^\circ}{4}\right) = 0{\cdot}9757$, $n = 1{\cdot}5215\ (23^\circ)$, viscosity = 2·4254 (25°)

Analysis: 0·1571 grm. substance gave 0·1824 grm. Ag_2S.

	Calc.	Found.	
S	15·39	15·02	%

6. Isoamylester $C_7H_7CSOC_5H_{11}$

A liquid of an intense yellow colour, B.P. = 155-158° under 32 mm pressure. $d\left(\frac{22^\circ}{4}\right) = 0{\cdot}9856$, $n = 1{\cdot}5252\ (23^\circ)$, viscosity = 2·2020 (22°)

Analysis: 0·1166 grm. substance gave 0·1267 grm, Ag_2S

	Calc.	Found.	
S	14·42	14·06	%

7. Benzylester $C_7H_7CSOCH_2C_6H_5$

An intensely yellow-coloured liquid, B.P. = 185-190° under 21 mm. pressure. $d\left(\frac{22^\circ}{4}\right) = 1{\cdot}0648$, viscosity = 3·8893 (22°).

Analysis: 0·1323 grm. substance gave 0·1344 grm. Ag_2S.

	Calc.	Found.	
S	13·23	13·14	%

VI Thionoxalic Esters.

1. Dimethylester $C_2S_2(OCH_3)_2$

Exactly analogous to the ester of monobasic thionic acids thionoxalic dimethylester was prepared from oxaliminodimethylester by the action of dry hydrogen sulphide.

It is a yellow liquid having a disagreeable odour and boiling at 50°-53° under 21 mm. pressure.

Analysis: 0·0603 grm. substance gave 0·1932 grm. Ag_2S.

	Calc.	Found.	
S	42·69	41·45	%

2. Diethylester $C_2S_2(OC_2H_5)_2$

A yellow liquid boiling at 80°-82° under 32 mm. pressure. $d\left(\frac{21^\circ}{4}\right) = 1{\cdot}0565$, viscosity = 1·1707 (21°).

Analysis: 0·1264 grm. substance gave 0·3511 grm. Ag_2S.

	Calc.	Found.	
S	35·98	35·93	%

3. Di-isopropylester $C_2S_2(OC_3H_7)_2$

This is also a yellow liquid which boils at 91°-93° under 43 mm. pressure.

Analysis: 0·0973 grm. substance gave 0·2327 grm. Ag_2S.

	Calc.	Found.	
S	31·09	30·94	%

As was pointed out by M. Matsui[1] and also by the writer[2] the reaction between these thionic ester and ammonia or amines in an ethereal solution differs from that in an alcoholic solution. In order to know whether the same generally holds true the reactions of thionic esters upon aniline and phenylhydrazine were examined, and it was found that such are always the case. When the ethylesters of thionacetic acid, thionpropionic acid, thionbenzoic acid and thionparatoluic acid were brought into reaction with aniline, they produced the corresponding thianilides in the ethereal solution and phenyliminoesters in the alcoholic solution. Reactions upon phenylhydrazine were also observed to proceed in an analogous manner, that is, thiophenylhydrazides of the formula $RCSNHNHC_6H_5$ were formed in the ethereal solution, and phenylhydrazones of the esters, $RC:NNHC_6H_5OC_2H_5$ in the alcoholic solution. The products were all confirmed by analysis, but it will be rather superfluous to describe the results in detail.

VII Thionic Acids.

1. Thionacetic acid CH_3CSOH

In the first communication[3] it was reported that thionacetic acid could only be isolated in an impure state when its ester was saponified with an aqueous caustic potash solution. Now it was found that the acid can be obtained with a better yield and in a purer state, if we use an alcoholic potash solution as the saponifying agent, and work taking great care to avoid high temperatures, and to exclude moisture.

The potassium salt formed by saponification was collected and repeatedly washed with absolute alcohol and then dissolved in water. Into the aqueous solution well cooled with ice dilute hydrochloric acid was added drop by drop, when a pale yellow substance separated out. The yellow substance was extracted with ether, and the ether was evaporated from the ethereal solution, previously well dehydrated with fused calcium

(1) Mem. Coll. Sci. Eng., Kyoto, **3**, 248 (1912).
(2) These Memoirs, **9**, 238 (1926)
(3) Loc. cit.

chloride, by passing a current of dry air.

Thionacetic acid is a pale yellow liquid which solidifies when cooled with a freezing mixture. It has a penetrating odour like that of acetic acid. In water it is not so soluble as acetic acid, but in ordinary organic solvents it dissolves well and gives a greenish-yellow-coloured solution. Its aqueous solution reacts strongly acidic. It is exceedingly unstable and changes into acetic acid and hydrogen sulphide even in the presence of a mere trace of water.

For analysis the amount of sulphur was determined as silver sulphide, thus:

0·0335 grm. substance gave 0·1081 grm. Ag_2S

	Calc.	Found.	
S	42·13	41·75	%

2. Thionpropionic acid C_2H_5CSOH.

This acid was isolated from its ethylester by a treatment similar to that described in the preparation of thionacetic acid. It is also an unstable yellow-coloured, mobile liquid having a penetrating odour.

Analysis: 0·1205 grm. acid gave 0·3308 grm. Ag_2S

	Calc.	Found.	
S	35·57	35·51	%

3. Thionphenylacetic acid $C_6H_5CH_2CSOH$.

This is a yellow crystalline substance insoluble in water. It has a characteristic odour and gradually decomposes, evolving hydrogen sulphide.

Analysis: 0·0601 grm. substance gave 0·0978 grm. Ag_2S

	Calc.	Found.	
S	21·07	21·05	%

4. Thionparatoluic acid $CH_3C_5H_4CSOH$

5. Thion-β-Naphtoic acid $C_{10}H_7CSOH$

These two acids are both solids of deep yellow colour. They were each analysed with the following results:

(1) 0·0395 grm. of the former gave 0·0647 grm. Ag_2S

(2) 0·0228 grm. of the latter gave 0·0302 grm. Ag_2S.

	Calc.		Found.		
	(1)	(2)	(1)	(2)	
S	21·07	17·04	21·19	17·14	%

6. Thionoxalic acid $C_2S_2(OH)_2$

This was obtained as a yellow crystalline substance by saponifying its di-ethylester with an alcoholic potash solution. It has a characteristic odour and is with difficulty soluble in water. Its properties were observed

to be quite similar to those of the monobasic thionic acids above described.

The results of ahalysis were as follows:

0·0132 grm. substance gave 0·0531 grm. Ag_2S

	Calc.	Found.	
S	52·49	52·04	%

The writer takes this opportunity of expressing his hearty gratitude to Professor M. Matsui for his kind assistance and advice in carrying out the work which was undertaken at his suggestion.

On Carbolthionic Acids and Their Esters. Part. III Carbithioic Acids and Esters.

By

Yoshihito Sakurada.

(Received December 22, 1925)

Abstract.

The only method hitherto known as a general mode of formation of the carbithioic acids RCS_2H has been that of Houben, which is to bring the Grignard reagent into reaction with carbon bisulphide.

Now it was found out by the writer of the present article that M. Matsui's method for the formation of carbolthionic acids may be well applicable for the preparation of the esters of carbithioic acid, and by saponifying these esters free acids may also be isolated.

The following esters and acids were experimentally confirmed to be thus prepared:

Esters:—Ethylester of methylbithioic acid, ethylbithioic acid, phenylbithioic acid, benzylbithioic acid, paratolylbithioic acid, β-Naphthylbithioic acid, and tetrathio-oxalic acid.

Acids:—Methylbithioic acid, ethylbithioic acid, phenylbithioic acid, paratolylbithioic acid and tetrathio-oxalic acid.

By using M. Matsui's[1] method for the preparation of carbolthionic esters the writer has succeeded in preparing thio-carbolthionic esters or esters of carbithioic acids which were for the first time prepared by Houben[2] and his collaborators. They prepared the acids first by the reaction[3] between the Grignard reagent and carbon bisulphide, and then esterified those acids with dialkyl sulphate. In the writer's method the

(1) Mem. Coll. Sci. Eng. Kyoto. **1**, 285 (1908); **3**, 247 (1912).

(2) Ber. **43**, 2481 (1910), **44**, 3228 (1911).

(3) Ber. **39**, 3219 (1906), **40**, 1303, 1725 (1907).

order of preparation was just the reverse, that is, esters were first prepared from thioimino-esters by the action of hydrogen sulphide, and these esters were then saponified with an alcoholic potash solution.

The experiment was conducted exactly in the same manner as in the preparation of carbolthionic esters by passing dry hydrogen sulphide into an ethereal solution of thio-iminoesters. As carbithioic esters thus formed further react upon ammonia, and change into the corresponding thiamides and mercaptanes, it is necessary to wash the ethereal solution promptly as soon as the reaction is over.

Methyl-carbithioic Ethylester

$CH_3CS_2C_2H_5$.

Into an ethereal solution of thioacetiminoethylester prepared according to the method of Pinner,[1] dry hydrogen sulphide gas was passed. The solution quickly began to take on an orange hue and at the same time white crystals of ammonium sulphide separated out. After sufficient hydrogen sulphide was passed, the ethereal solution was repeatedly washed with water completely to get rid of the hydrogen sulphide, ammonia and ammonium sulphide, and dried with fused calcium chloride. A mobile orange liquid obtained on evaporation of the ether was distilled, and the portion boiling at 128°-132° was collected and analysed.

0·0852 grm. substance gave 0·3488 grm. Ag_2S

	Calc.	Found.	
S	53·34	52·96	%

The orange liquid left on evaporation of the ether was sometimes found to contain some crystals of thioacetamide. This would perhaps be the product of the reaction of the ester upon ammonia which might have still been contained in the ethereal solution without being thoroughly washed away.

The properties of the methylbithioic ethylester thus prepared were found mostly to agree with those described by Houben.[2] It does not fume in a moist atmosphere as some carbolthionic esters do. Its specific gravity[3] and index of refraction were determined as follows:

$$d\left(\frac{28^\circ}{4}\right) = 0{\cdot}9807, \quad n = 1{\cdot}5303\ (28^\circ)$$

Ethylcarbithioic Ethylester.

$C_2H_5CS_2C_2H_5$

This was prepared from thiopropioiminoethylester by treating its

(1) Ber. **16**, 352 (1883).

(2) Loc. cit.

(3) Houben found it to be $d^{16}=1{\cdot}036$

ethereal solution with hydrogen sulphide. It is an orange-coloured mobile liquid boiling at 150°-155°. The following physical constants were determined:

$d\left(\frac{27^\circ}{4}\right) = 0{\cdot}9711$, $n = 1{\cdot}5259\ (27^\circ)$ viscosity $= 2{\cdot}1535\ (27^\circ)$.

Analysis: 0·1481 grm. substance gave 0·5450 grm. Ag_2S

	Calc.	Found.	
S	47·77	47·61	%

Phenylcarbithioic Ethylester.

$C_6H_5CS_2C_2H_5$

This was obtained from thiobenziminoethylester as a red liquid boiling at 122°-125° under 72 mm. pressure. It was analysed with the following results:

0·1427 grm. substance gave 0·3952 grm. Ag_2S

	Calc.	Found.	
S	35·18	35·83	%

Benzylcarbithioic Ethylester.

$C_6H_5CH_2CS_2C_2H_5$

This is an orange-coloured liquid boiling at 140°-144° under 45 mm. pressure. Its specific gravity and viscosity were determined as follows:

$d\left(\frac{29^\circ}{4}\right) = 1{\cdot}0462$ viscosity $= 2{\cdot}9831\ (29^\circ)$.

Paratolylcarbithioic Ethylester.

$CH_3C_6H_4CS_2C_2H_5$

Collecting the portion distilled off at 160°-165° under 85 mm. pressure, the following physical properties were determined:

A liquid of a red colour, $d\left(\frac{27^\circ}{4}\right) = 1{\cdot}0085$, viscosity $= 2{\cdot}3215\ (27^\circ)$

Analysis: 0·1373 grm. substance gave 0·3487 grm. Ag_2S

	Calc.	Found.	
S	32·67	32·86	%

β-Naphthylcarbithioic Ethylester.

$C_{10}H_7CS_2C_2H_5$

This was prepared from thio-β-naphtoiminoethylester as a thick liquid of a deep red colour boiling at 200°-205° under 45 mm. pressure.

Analysis: 0·1260 grm. substance gave 0·2622 grm. Ag_2S

	Calc.	Found.	
S	27·60	26·92	%

Tetrathio-oxalic Ethylester.

$C_2S_2(SC_2H_5)_2$

Thio-oxaliminoethylester prepared by passing cyanogen and hydrogen

chloride simultaneously into an ethereal solution of ethyl mercaptane was treated with hydrogen sulphide in the usual manner. The portion boiling at 90°-93° under 43 mm. pressure was examined.

It is an orange-coloured liquid having a disagreeable odour and is insoluble in water. Its properties resemble those of the esters of monocarbithioic acids in every respect.

The results of analysis were found as follows:

0·0938 grm. substance gave 0·4390 grm. Ag_2S.

	Calc.	Found.	
S	60·97	60·55	%

All the esters above described could without any difficulty be saponified with an alcoholic potash. It was, however, a very difficult task to collect them in a pure state and in quantities sufficient for close examination.

The following are the bithioic acids thus isolated:

Methylbithioic Acid. CH_3CS_2H

Methylbithioic ethylester was mixed with an alcoholic potash solution and left to stand for a few days with an occasional shaking, when the acid formed by saponification precipitated as its potassium salt. The precipitates were collected, well washed with alcohol and then dissolved in water. On cooling the aqueous solution with ice it was acidified by adding dilute hydrochloric acid drop by drop. A yellow substance thus separated out in the solution was extracted with ether, and into the ether extract, after having been well dehydrated with fused calcium chloride, a current of dry air was passed to drive off the ether.

The bithioic acid was obtained as an orange-coloured oily substance having a disagreeable penetrating odour. It is not so soluble in water as acetic acid.

For confirmation the quantity of sulphur was determined.

0·0610 grm. substance gave 0·3270 grm. Ag_2S.

	Calc.	Found.	
S	69·57	69·35	%

Ethylbithioic Acid $C_2H_5CS_2H$

This was obtained as an orange-coloured oil by saponifying ethylbithioic ethylester with alcoholic potash.

Analysis: 0·0112 grm. substance gave 0·0522 grm. Ag_2S

	Calc.	Found.	
S	60·39	60·29	%

Phenylbithioic Acid $C_6H_5CS_2H$

This is a red-coloured thick oil having a penetrating odour. Its solution in organic solvents is also coloured red.

Analysis: 0·0252 grm. substance gave 0·0809 grm. Ag_2S.

	Calc.	Found.	
S	41·58	41·53	%

Benzylbithioic Acid $C_5H_5CH_2CS_2H$

A thick orange liquid having a penetrating odour.

Analysis: 0·0168 grm. substance gave 0·0491 grm. Ag_2S.

	Calc.	Found.	
S	38·12	37·81	%

Paratolylbithioic Acid $C_7H_7CS_2H$

This is a thick red liquid with a penetrating odour. It was analysed with the following results:

0·0229 grm. substance gave 0·0677 grm. Ag_2S.

	Calc.	Found.	
S	38·12	38·25	%

Tetrathio-oxalic Acid $C_2S_2(SH)_2$

This was isolated as an orange-coloured viscous liquid by saponifying its ethylester with alcoholic potash. Though it is only with difficulty soluble in water, it is very soluble in the ordinary organic solvents to which it imparts a yellow colour.

Analysis: 0·0151 grm. substance gave 0·0968 grm. Ag_2S.

	Calc.	Found.	
S	83·13	82·93	%

The writer wishes to express his hearty gratitude to Professor M. Matsui for his kind assistance and encouragement throughout the work.

Catalytic Action of Reduced Copper on Pinacones.

By

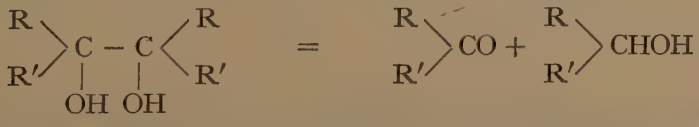
Shozo Yamaguchi.

(Received February 2, 1926)

In the recent article[1] on the catalytic action of reduced copper on oximes, it was already stated by the present writer that reduced copper heated at 200° acts on the oximes to promote, on the one hand, reduction like reduced nickel, and on the other, Beckmann's rearrangement, and the latter action was noticed to be similar to that of dilute sulphuric acid on oximes.

Hence, it may naturally be anticipated that the reduced copper is also capable, under certain conditions, of excercising a catalytic influence on the transformation of pinacones into pinacolines, which was actually observed by many investigators in the case of the action of dilute sulphuric acid on pinacones.

According to W. Thorner and Th,. Zincke[2], the pinacones derived from benzophenone and acetophenone, when heated above their melting points (280°−300°), deconposed completely into the corresponding ketone and alcohol as will be shown in the following scheme:



It seems, therefore, an interesting problem from the view point of the contact action, to see what chemical change would take place when these

1 These Memoirs, **9**, 427 (1926).
2 Ber. D. Chem. Ges., **13**, 641 (1880).

pinacones come into contact with reduced copper heated at about 200°, and the present experiment was undertaken to learn the catalytic action of this metal and also to obtain some facts which might throw some light upon the mechanism of the pinacoline transformation.

1. Benzophenone pinacone.

The pinacone of a m.p. of 168°—169°, prepared from benzophenone by reduction with zinc and sulphuric acid in an alcohol solution, according to the directions of Ed. Linnemann[1] and W. Thorner & Th. Zincke,[2] was passed on reduced copper heated at 200°, and the reaction products remained almost entirely on the catalyst, due to their non-volatility, treated with chloroform and separated from the catalyst by filtration. The product, thus obtained, amounted to 8 grm., from 10 grm. of the pinacone, which was ascertained to be composed of 7 grm. of pure benzophenone pinacoline with a m.p. of 177°—179°, after being purified by the method suggested by C. Paar[3].

On analysis, it gave the following results:

0.1122 grm. subst. gave 0.3674 grm, CO_2 and 0.0576 grm. H_2O

	C.	H.
Found.	89·30	5·74
Calc. for $C_{26}H_{20}O$	89·63	5·77

For confirmation, 4 grm. of the pinacoline were hydrolysed with an alkali solution into 3 grm. of pure triphenyl methane (m.p, 92°—93°) and 1·0 grm. of pure benzoic acid (m.p. 121°), and both substances were confirmed by determination of the chemical and physical properties and also by the elementary analysis:

0.1135 grm. of the hydrocarbon gave 0·3867 grm. CO_2 and 0.0687 grm. H_2O.

	C.	H.
Found.	92·92	6·77
Calc. for $C_{19}H_{16}$	93·42	6·58

0.1099 grm. of the acid gave 0·2773 grm. CO_2 and 0.0502 grm. H_2O.

	C.	H.
Found,	68.70	5·11
Calc. for $C_7H_6O_2$	68·84	4·92

1 Lieb. Ann., **133**, 26 (1865).
2 Ber. D. Chem. Ges., **10**, 1473 (1877).
1 Ber. D. Chem. Ges., **17**, 911 (1881).

Thus, the pinacoline which was obtained by the contact action of reduced copper on benzophenone pinacone, was confirmed to be the same substance which was previously obtained by other chemists[1] from the same pinacone by means of acetyl chloride, benzyl chloride, dilute sulphuric acid oxalic acid and concentrated hydrochloric acid heated above 200°.

2. ACETOPHENONE PINACONE.

Applying the contact action of reduced copper at 130°—140° on 13 grm of acetophenone-pinacone, m. p. 120°, prepared from acetophenone[2], 6 6 grm. of liquid and 4 grm. of solid reaction products were obtained.

The liquid reaction product consisted of the following fractions:

1. 140°—160° trace.
2. 160°—205° 3·0 grm.
3. Residue 2·4 grm.

And the second fraction was confirmed to consist mainly of acetophenone by oximiration with hydroxylamine, and the residue and also the solid reaction product above mentioned were noticed to be composed mostly of the pinacone (m. p. 120°) unchanged in the reaction.

In the second reaction of the pinacone carried out at higher temperature, such as 180° and 200°, no other chemical reaction differing from that mentioned previously could be observed.

Such a difference in the behavior of the pinacones toward reduced copper heated at about 200°, would be ascribed either to the chemical affinity between two tertiary carbons of the pinacones molecule or to some other reason, and further experiments are required to discover an explanation which will cover the fact underlying the pinacoline transformation, one of the most interesting problems in modern organic chemistry.

Sep. 1925 Laboratory of Organic and Bio-chemistry.

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1 W. Thorner & Th. Zincke: Loc. cit. C. Paar: Loc. cit. E. Erlenmeyer: Ber. D. Chem. Ges., **14**. 322 (1881). U. Nef: Lieb. Ann., **355**, 243 (1904); **318**, 37 (1901); H. Meerwein: Lieb. Ann., **376**, 152 (1910); **396**, 200 (1913); **405**, 129 (1914); **417**, 255 (1918); **419**, 121 (1919). F. Henrich: Theorien der Organischen Chemie 5 Auflage 1924 S. 444.

2 Ber. D. Chem. Ges., **10**, 1714 (1877).

On the Relative Ignition Temperatures of Solid Fuels.

By

Kenji Nakamura and Akira Shimomura.

(Received March 31, 1926)

Abstract.

Twenty-two kinds of solid fuels, including lignites, bituminous as well as anthracitic coals of oriental origin, semi-coke, metallurgical coke and wood-charcoal were tested for their relative ignition temperatures in the sense of Wheeler's definition.

A special form of heating tube with a paraffin-bath fused in was used, and was found to give more uniform heating than the ordinary tube such as Wheeler used.

Wheeler's general conclusion that the higher the oxygen content of the coal, the lower the relative ignition temperature has been confirmed with most of the coals we examined. We found, moreover, that the volatile matter and ash-contents of the fuel have a decided influence on their relative ignition temperatures, that is, generally a high volatile or a low ash-content gives a low ignition temperature, provided the other conditions remain equal.

In connection with the spontaneous combustion of coal and its combustibility, the ignition temperature of coal has been studied by many investigators under various conditions, among whom Wheeler[1], Arms[2], Sinnatt, Moore and Slater[3] have recently published interesting results relating thereto. None of the methods proposed, however, is entirely satisfactory for the determination of the *ignition temperature* of the solid fuel, the definition of which itself is by no means absolute at the present. In the circumstances, we experimented in the light of Wheeler's method (*l. c.*) which we thought very practical and easy to copy. He declares that

1 J. Chem. Soc., **113**, 945 (1918); Fuel, **3**, 366 (1924).
2 Bull. 128, Univ. Illinois (1922).
3 J. Soc. Chem. Indust. **39**, 72T (1920); Fuel, **2**, 211 (1923); **4**, 194 (1925).

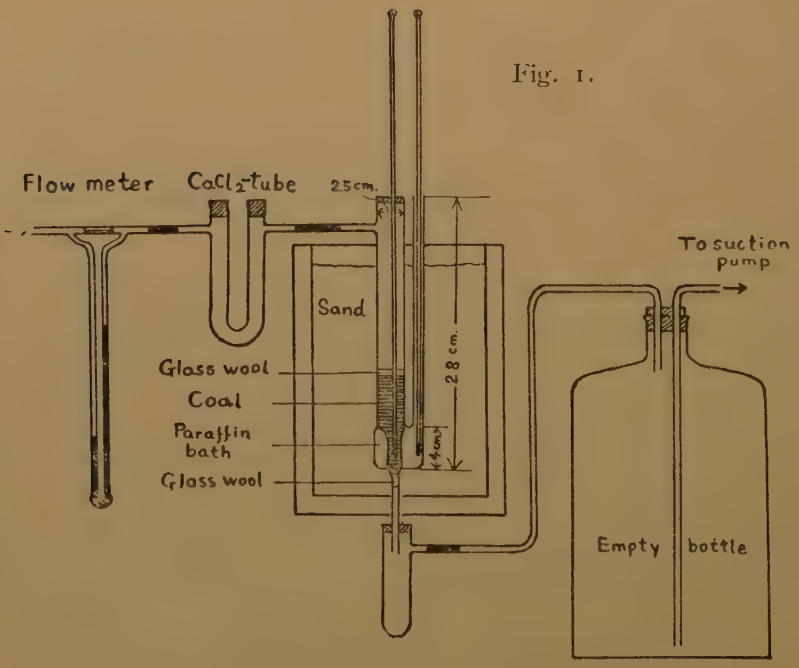
"from a practical as well as from a theoretical point of view, it is sufficient to know at what temperatures, under standard conditions, different coals begin to react with oxygen so rapidly that the ultimate appearance of flame is assured," and proposes a method to heat the coal powder by means of a sand-bath under specified conditions, and note the rise of temperatures of both the coal and the bath, the latter always higher than the former at the beginning of the experiment The temperature of the coal rising more rapidly than that of the bath, reaches the same temperature as the latter in due course, and finally exceeds it. The point at which both the coal and the sand-bath assume the same temperature is taken to be the ignition temperature of the coal relative to other coals tested in the same way.

Description of the Apparatus and the Method of Operation :—

Taking into consideration all the governing experimental factors, such as degree of fineness of the coal powder, the rate of the air current, the height of the coal column, the diameter of the heating tube, the position of the thermometer bulbs and the influence of the heating medium, we resorted to the following method.

Twenty grams of powdered coal (50—80 mesh) were put into a

Fig. 1.



glass tube as shown in Fig. 1, which is a mobified form of Wheeler's original tube. It was found to offer the advantage of more uniform heating owing to the presence of a paraffin-bath secondarily heated by the electrically heated sand-bath.

While a current of dry air was passed at a constant rate of 1100 c. c per minute, the temperature of the sand-bath was slowly raised as uniformly as possible in each experiment, and simultaneous readings of two thermometers, one in the coal column, and the other in the paraffin-bath, were taken at frequent intervals.

In this manner two time-temperature curves are obtained, one showing the rate of rise of temperature of the paraffin-bath, and the other that of the fuel. These two curves usually cross at a definite point, or the relative ignition temperature, characteristic of the fuel.

Fig. 2.

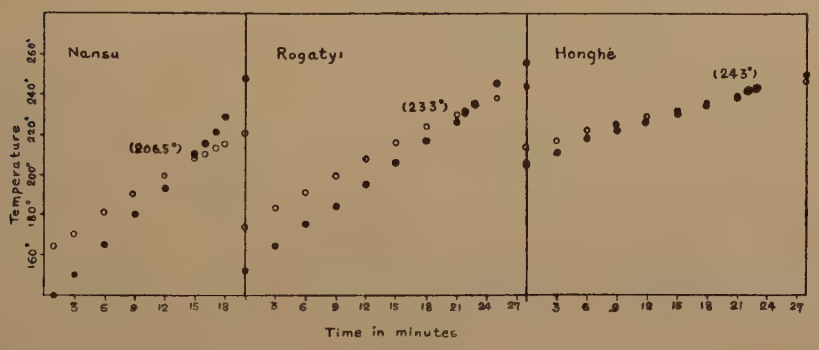


Fig. 2 shows the general form of the curves with three typical coals, Nansu (bituminous, vol. matter 30·84%) Rogatyi (semi-anthracitic, vol. matter 19·17%) and Honghé (anthracitic, vol. matter 10·00%). Generally bituminous coal, when it reaches its ignition temperature, shows so sudden a rise of temperature that often the hard glass tube may be fused in a few minutes, — in other words, the crossing of the two curves is very sharp. As for the anthracitic coal, not only is the relative ignition temperature very high, but the rate of self-heating of the coal is very much slower in comparison to other types of coal,— or the two curves do not cut each other as sharply as in the case of bituminous coals. There are, of course, intermediate forms between them.

Twenty-two kinds of solid fuels, including various types of coal, semi-coke, metallurgical coke and wood-charcoal were tested for their relative ignition temperatures and the results are summarised in the following table, together with the analyses of the fuels showing their percentage of volatile

matter, ash and oxygen contents.

	No.	Solid fuel	Analyses: Volatile-matter (dry basis) %	Ash (dry basis) %	Oxygen (dry, ashless basis) 100−(C+H+N)%	Relative ignition temp. °C
Lignites	1	Ten-tan	32·73	11·53	21·03	215
	2	Mgach 3ft	35·70	2·34	23·77	221
Bituminous Coals	3	Yubari No. 1 pit	43·39	10·69	11·74	216
	4	Koyaki	38·88	8·78	10·85	224
	5	Sakito	37·23	12·14	11·63	221
	6	Nansu	30·84	3·73	13·16	206·5
	7	Hashima	33·74	6·75	9·27	225
	8	Matsushima	33·57	12·63	12·93	218
	9	Besshu	32·81	11·70	6·56	228
	10	Sasa	30·80	13·99	8·92	222
Semi-anthracitic Coals	11	Kaiping	27·47	13·43	13·22	213
	12	Dui	24·69	5·03	11·46	221
	13	Poshan	20·02	11·27	5·40	244
	14	Rogatyi	19·17	9·56	5·64	233
Anthracites	15	Honghé	10·00	12·83	3·42	243
	16	Tsun-chin	8·75	11·85	5·83	241
	17	Kin tshou	7·68	13·95	3·21	231
	18	Mallien	3·52	16·61	2·74	347
Semi-Coke & coke	19	Semi-coke (Yubari No. 1 pit)	14·87	11·04	9·94	223
	20	Coke (Yubari No. 1 pit)	1·70	15·29	0·27	too high to measure
Wood charcoal	21	Charcoal (soft)	16·46	0·85	8·34	208
	22	Charcoal (hard)	5·10	3·41	5·01	230

It is known that coals that most readily self-heat are those containing the highest proportion of oxygen. As shown in Fig. 3a, this was found true with most of the fuels we examined, with occasional exceptions. So far as we have examined, this rule does not seem to hold with lignites, the oxygen content of which exceeds 20%.

Although not so distinct as the oxygen content, the volatile matter

Fig. 3a.
Fig. 3b.
Fig. 3c.
Relative Ignition Temperature.
200°
210°
220°
230°
240°
250°
↑347°
↑347°
↑347°
5
10
15
20 %
Oxygen-content
10
20
30
40 %
Volatile Matter
5
10
15 %
Ash-content.

and ash contents of the fuel were found also to exert a decided influence on its relative ignition temperature as shown diagrammatically in Figs 3b and 3c, contrary to Wheeler's conclusion that "no relationship exists between the ignition temperature now recorded and other (than oxygen content) analytical data."[1]

Hence, in general, the greater the oxygen content or volatile matter, or the less ash content tends to lower the relative ignition temperature of the solid fuel if other factors remain constant. On closer examination, it will be found that those the ignition temperatures of which deviate from the general trend have always a more prominent effect of other factors than the one in question.

Prof. J. Yonezawa of the Osaka Higher Technical School examined the relationship between the relative ignition temperatures and the amount of pyridine extract with several Hokkaido coals and Hokoku coals (unpublished), and came to the conclusion that the coals that yield less extract generally show lower ignition temperatures. We wish to take this opportunity to thank Prof. Yonezawa for kindly giving us his data on this subject.

In conclusion we offer our cordial thanks to Prof. M. Chikashige for his interest in this work.

1 J. Chem. Soc., **113**, 953 (1918).

On the Arrangement of the Micro-crystals in Silver deposited by Electrolysis.

By

Hideki Hirata and Hisaji Komatsubara.

(Received March 16, 1926)

Abstract

The arrangement of the micro-crystals in silver deposited electrolytically was examined with X-rays. The X-ray-patterns were seen to be explainable with the consideration that the micro-crystals have a tendency to deposit in a fibrous form, and that the diagonal axes of the cubic crystals of silver are arranged parallel to each other as the axis of the fibrous form.

Introduction.

Ever since the ibeas of Laue and Braggs have successfully been realized by experiments, a wide field of investigation bas been opened up in connection with the diffraction phenomena of X-rays by crystals. As one of the extensions of these ideas, the arrangement of the micro-crystals existing in substances has become a subject of the keenest researches. From these researches, it has become evident that the arrangement of the micro-crystals in metals depends largely upon the history of the specimen. Thus, it seems to be of fundamental importance to examine the specimen prepared after some process of a simple and clear nature such as electrolysis, as was the case with Glocker and Kaupp[1] and with Bozorth[2].

So, the writers were also induced, at the kind suggestion of Prof. Masumi Chikashige, to repeat the experiments on the same line with electrolytically deposited silver. Their results are briefly described in the following pages.

1 Z. S. f. Phys., **24**, 121 (1924).

2 Phys. Rev., **26**, 390(1925).

Specimen.

The specimens used were silver electrolytically deposited on a rolled silver plate. Their macro-structures as shown in Plate V, are mossy (Fig. 3, and Fig. 4) or acicular (Fig. 5) according to the conditions of the electrolysis. For the sake of abbreviation, let us call the mossy one specimen A, and the acicular, specimen B, respectively. In the same plate, the micro-structure of these two kinds of specimen are reproduced (Fig. 6, and 7). The conditions under which they were prepared are given below :—

Specimen A :

Electrolyte : 5.5% Ag and 1% free nitric acid.

Potential difference : 1.5 volt.

Current density : 0.02 Amp./cm^2.

Anode : Iron plate thinly covered with Japanese lacquer.

Nineteen vats, each of 60 cms. cube, were arranged in 2 lines; the electrolyte 5.2 cms. deep was flowing from one vat to another at the rate of 6.6 liters per minute. The crystals came to appear after 3 days equally in all the vats.

Specimen B :

Electrolyte (some quantity of silver nitrate being added to the residual liquid in the first experiment) : 7.5% Ag. and 0.75% free nitric acid.

Potential difference : 1.5 volt.

Current density : 0.02 Amp./cm^2.

One vat only was used without any flow of the liquid.

Experimental Part.

Outline of the Experimental Method : — In the present experiment, the writers adopted the ordinary "transmission method" founded by Keene[1], Nishikawa[2], and others.

The X-rays emitted from the molybdenum anticathode of a U-type Coolidge tube were cut down by two parallel lead diaphragms. Each of these diaphragms has a circular hole and a narrow pencil of X-rays passing through these holes was made to strike the specimen to be tested. The photographic plate was placed perpendicularly to the incident beam in a position a few cms. behind the specimen.

To excite the tube, a transformer was employed. The maximum voltage measured by the length of a spark gap between needle-points was

1 Phil. Mag., **26**, 712 (1913).

2 Proc. Tokyo Math. Phys. Soc., **7**, 131 (1913).

about 50–70 K. Vs., and the current through the tube was 4–5 milliamperes. The time of exposure varied from 27 to 32 hours according to the condition.

Discussion of the Experimental Result:

(i) Specimen A: Some finest fragments, of this specimen with which the experiment was first performed, had been pasted on a sheet of paper, so that the face of each lamella was parallel to the surface of the paper. When the common face of these lamellae, which coincided with the surface of the paper, was set perpendicular to the incident beam, then the interference figure reproduced in Fig. 8, Plate VI was obtained on the photographic plate placed 3.2 cms. behind the specimen.

In this figure, the prominent part of the blackening consists of a number of concentric circular rings, and the central spot impressed by the undeflected beam.

It is evident that the interference figure under consideration is essentially the same as those obtained by Debye-Scherre, and Hull by the powder method: the concentric rings are considered to be produced when the arrangement of the micro-crystals in the specimen has no regularity with regard to the direction of the incident beam.

If we inspect Fig. 8 more minutely, it will be observed that this figure consists of a large number of bands radiating outward from the central spot, and that, the concentric rings in the figure are nothing but an assemblage of a large number of intense spots on the radiating bands. This point seems to be a little different from the figure obtained by the ordinary powder method, and the reason will be given later on.

Fig. 12 and Fig. 9 are the interference figures taken in a similar way as Fig. 8 with a larger fragment of specimen A. To obtain these two figures, a piece of the mossy crystal of moderate size (0·8–1·2 mms. in dia.), and a very large piece which was rather foliate (about 4 mms. in width) were used, respectively. As in the previous case, the photographic plate was placed 3·2 cms. behind the specimen in both cases.

The prominent parts of these two figures, Fig. 12 and Fig. 9 consist of several bands radiating outward from the central spots. In the former figure, there are 6 prominent linear bands, any one of them making an angle of about 60° with the neighbouring bands on either side; while the latter figure consists of 24 prominent wide radiating bands of rather triangular shapes. On the whole, they present the symmetrical interference figures, and each of them has a unmber of intense spots on it, which seem to be registered by the characteristic radiations

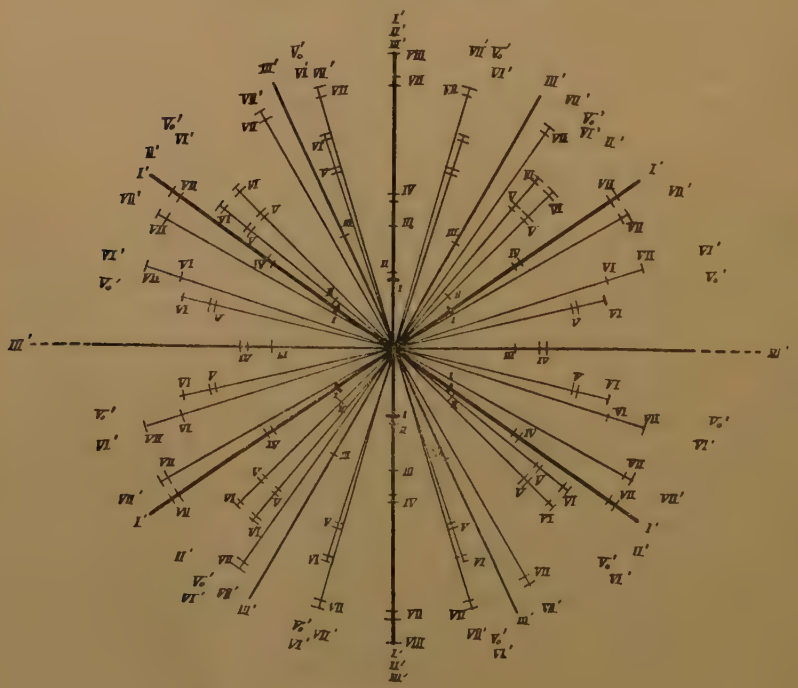
from the target.

It will easily be noticed by putting Fig. 12 upon Fig. 9 that 6 prominent bands in Fig. 12 coincide with the central lines of the most intense triangular shaped bands in Fig. 9 which are denoted by I' in the figure. Moreover, by reducing the diameters of the slits to about 0·8 mms., the same interference figures as Fig. 12 were also obtained, even when a piece of the large foliate crystal was used. These facts show that there must exist some connections between the arrangements of the micro-crystals of the two samples to give rise to the two different figures under consideration.

It can also be noticed that the distance from the central spot to any one of the intense spots in Fig. 12 and Fig. 9 is equal to the radius of one of the concentric rings represented in Fig. 8, Plate VI. This equality of distances suggests the existence of some relations between these figures.

The annexed Fig. 1, represents diagrammatically the central lines of the radiating bands in Fig. 9 as well as the positions of the intense spots on the bands. In this figure, the intensity of each band is shown by the thickness of the corresponding line. As the first approximation,

Fig 1. The Standard Figure.



the lines representing the position of the central lines of the triangular bands were drawn as straight lines because the curvature was insignificant.

Now suppose that there is an arrangement of micro-crystals which will induce the interference figure characterized by the condition, that all the radiating bands in this figure are nearly linear, and that the distribution of the radiating bands are those given in Fig. 1. For the sake of convenience, we shall call all the figures, the same as that represented in Fig. 1, the "standrad figures."

In the standard figures, it will be noticed that the intense spots represented by 1' coincide with the radiating bands reproduced in Fig. 12, Plate VII. Moreover, the same figures as Fig. 8, and Fig. 9, in Plate VI, can be obtained by overlapping many of these standard figures: To get the same figure as Fig. 9, the many standard figures should be placed one upon another in such a way that the central spot of each figure coincides with the others, and that all the correspoding radiating bands in the figures are displaced a little, within about 5°. The same figure as Fig. 8 can be realized, when these standard figures are irregularly overlapped by keeping their central spots on the same point.

From the above consideration, it may be quite possible to suppose that the arrangement of the micro-crystals to produce the standard figure and those to produce Fig. 8, Fig. 9, and Fig 12, are essentially the same.

At this stage it may be well to note the condition under which such a standard figuer is produced. As is already known, the radiating bands are produced only when the specimen is fibrous; i. e., the micro-crystals in the specimen are mostly so arranged that a certain definite axis of every crystal is arranged in the same direction, but that in other respects the orientation is at random.

As a result of many researches with such fibrous specimens, the following facts are also well known:

(a) If the axis of the fibrous arrangement is placed perpendicularly to the direction of the incident beam, the figure consists of a set of nearly straight bands passing through the central spot; (b) If, however, the axis is inclined against the plane normal to the incident ray, the figure is altered; the radiating bands in this figure are not nearly straight but are γ shaped; (c) In the extreme case, when the axis of the fibre is brought parallel to the incident ray,the figure obtained is a set of concentric rings around the central spot.

Thus considered, it will easily be seen that the orientation (a) of the fibrous arrangement applies well to the case which will give rise to the standard figure.

The intense bands in the standard figure, as already stated, coincides well with Fig. 12, Plate VII. It would seem, accordingly, to be presumable that the latter figure would also be obtained by the orientation (a),

Thus, it seems to be quite legitimate to accept the following two statement:—

(1) The micro-crystals in the moderate sized lamella are mostly so arranged that they have a definite common axis, and any reflection plane is inclined with a definite angle to the direction of this axis, but that in other respects the orientation of the reflecting plane is irregular.

(2) The direction of the common axis is perpendicular to the direction of the incident ray. Therefore, the common axis should be situated on the face of the lamella.

As was stated before, the photograph, Fig. 8 was obtained with a specimen consisting of a large number of fine lamellae. If we assume that each lamella in this case contains micro-crystals of the same fibrous arrangement as that in a moderate sized lamella, then Fig. 8 is capable of immediate explanation.

Now, before entering into details, let us determine the indices of each atomic plane, by the reflection of which the concentric rings are formed.

From the researches of Vegard[1], Kahler[2], Gerlach[3], it is known that the crystal of silver is of a face-centred cubic lattice, the one side of the elementary cube being 4.06 A. U, long. From these data, the spacing of each atomic plane can be calculated.

In Table 1, the indices of the prominent atomic planes, and the calculated values of the corresponding spacings d are represented.

Table. 1.
The Calculated Values of d.

Indices of Planes	d in 10^{-8} cm.
(111)	2·34
(100)	2·03
(110)	1·44
(210)	0·91
(211)	0·83

The numerical values of d can also be caluclated from the radii of the concentric rings in Fig. 8. If we denote the value of a spacing by d, the wave length of the characteristic radiation giving rise to a ring by λ, the distance of the photographic plate from the sample by L and the radius of a ring by r, then we have the following weell known relations between them.

$$2\,d\sin\theta = n\lambda \quad \ldots\ldots(1)$$

$$L\tan 2\theta = r \quad \ldots\ldots(2)$$

1 Phil. Mag., **31**, 83 (1916).
2 Phys. Rev., **8**, 210 (1921).
3 Z. S. f. Phys., **9**, 184 (1922).

where n is a positive integer representing the order of the spectrum, and $\theta = \frac{\pi}{2} - \gamma$ is the glancing angle.

Now for the sake of convenience, let us denominate the concentric rings by I, II, III, IV, V, VI, VII and VIII respectively in order of increasing radius. By measuring the radii of these rings, we obtain the numerical values of r as shown in the second column of Table 2. If we substitute these numerical values of r, and L = 3.2 in equation (2) successively, the value of θ corresponding to each ring will be obtained. The values of θ thus calculated are given in the third column of Table 2. With these values of θ the values of $\frac{d}{2}$ which are given in the fourth column of Table 2, will be found from equation (1) by assigning to λ the value of the wave length of the Kα line of molybdenum. Though it may be possible that the Kβ line of molybdenum will also appear, but as the intensity of this line is very feeble compared with that of the Kα line, we have taken

Table. 2.

No. of Rings	r in cm.	θ	$\frac{d}{n}$ in cm.	n	d in 10^{-8} cm.	Calculated Values: d in 10^{-8} cm.	Calculated Values: Indices of Planes	Indices of the Reflecting Planes
I	1·01	8°46′	$2{\cdot}33^{9}$	1	2·34	2·34	(111)	$(111)_{I}$
II	1·17	10° 3′	$2{\cdot}03^{3}$	1	2·03	2·03	(100)	$(100)_{I}$
III	1·79	14°37′	$1{\cdot}40^{6}$	1	1·41	1·44	(110)	$(110)_{I}$
IV	2·26	17°37′	$1{\cdot}17^{5}$	2	2·35	2·34	(111)	$(111)_{II}$
V	2·77	20°26′	$1{\cdot}01^{6}$	2	2·03	2·03	(100)	$(100)_{II}$
VI	3·29	22°54′	$0{\cdot}91^{2}$	1	0·91	0·91	(210)	$(210)_{I}$
VII	4·03	25°47′	$0{\cdot}81^{6}$	1	0·82	0·83	(211)	$(211)_{I}$
VIII	4·44	27° 7′	$0{\cdot}77^{9}$	3	2·34	2·34	(111)	$(111)_{III}$

the Kα line only. For the value of the wave length of the Kα line, we have given the mean value of the $K\alpha_1$ and $K\alpha_2$ lines, which is equal to $\lambda\alpha = 709.73 \times 10^{-11}$ cm.

Each one of the unmerical values of $\frac{d}{n}$ in the fourth column of Table 2, should represent a spacing or its submultiple of the silver crystal. Consequently, by assigning an adequate positive integer to n, the numerical value of d will be obtained from each one of the values of $\frac{d}{n}$.

Now assigning to n the integers as shown in the fifth column of Table 2, the numerical values of d in the sixth column are obtained. As was to be expected, each one of these numerical values agrees well with one of the calculated values in Table 1, which are here rewritten in the seventh column of Table 2. The indices of the atomic planes corresponding

to the spacings given in the seventh column — and consequently in the sixth column — of Table 2 are tabulated in the eighth column. Thus it seems to be legitimate to assign the indices of the atomic planes and the order of the spectra as given in the ninth column to each concentric ring. The symbols ( )I, ( )II, and ( )III in the ninth column denote the order of the spectrum.

Next, let us determine separately the indices of the atomic planes which are responsible for causing the radiating bands. This determination was attempted in the same way as performed by S. Tanaka[1], and T. Fujiwara[2] who made use of the position of the intense spots on each radiating band.

In Table 3, the first column represents the numbers of the radiating bands marked in Fig. 9, Plate VI, or in Fig. 1. The numbers of the intense spots on each radiating band are given in the second column. Here it must be noted that the intense spot is denoted by the same numbes as that of the correspondind concentric ring.

Table. 3.

No. of Radiating Bands	No. of Intense Spots	Indices of the Planes
III′	III, IV,	$(1,1,0)_{I}$
V$_o$′	V, VI,	$(3,3,1)_{I}$
VI′	VI, VIII,	$(2,1,0)_{I}$
VII′	VII,	$(2,1,1)_{I}$
I′	I, IV, VII,	$(1,1,1)_{I\ II}$
II′	II, V, VI,	$(1,1,0)_{I}$
V$_o$′ VI′	V, VI,	$\begin{cases}(2,1,0)_{I}\\(3,3,1)_{I}\end{cases}$
VII′	VII,	$(2,1,1)_{I}$
III′	III,	$(1,1,0)_{I}$
V^o VI′	V, VI,	$\begin{cases}(2,1,0)_{I}\\(3,3,1)_{I}\end{cases}$
VII′	VII,	$(2,1,1)_{I}$
I′ II′ III′	I, II, III, IV, VII, VIII	$\begin{cases}(1,0,0)_{I\ II}\\(1,1,0)_{I\ II}\\(1,1,1)_{I\ II\ III}\end{cases}$

The orders of the spectrum and the indices of the atomic planes belonging to these spots should be the same as those of the corresponding concentric rings, These were already given in Table 2, and they are tabulated again in the third column of Table 3. It is clear that the atomic plane which gives rise to the intense spots on a radiating band should also give rise to this radiating band. Consequently, we can regard the indices of the atomic planes given in the third column of Table 3 as those giving rise to the bands represented in the first column of the same table.

From the angular distribution of the radiating bands the axis of the micro-crystals arranged in the direction of the axis of the fibre will be determined. For this purpose a calculation was carried out as was done

1 These Memoirs, **8**, 319 (1925).
2 These Memoirs, **8**, 339 (1925).

by A. Ono,[1] who made use of the following relation.

$$\cos\beta = \cos\gamma \cos\alpha + \sin\gamma \sin\alpha \cos\varphi \quad \ldots\ldots\ldots\ldots(3)$$

where α is the angle between the incident ray and the fibrous axis of the crystals, β the angle between the normal of a certain reflecting plane and the fibrous axis of the crystals, γ the angle between the incident ray and the normal of the reflecting plane, and φ the azimuth of a point on a radiating band measured on the photographic plate, from the direction parallel to the fibrous axis of the crystals by taking the central spot as the pole.

From the above relation (3) and equation (2), each radiating band will be traced out, for a definite value of α and β, by giving various values to γ, and the by finding the numerical relations between φ and r. It will easily be seen that, when $\alpha = \frac{\pi}{2}$ at the vicinity of the central spot, the radiating bands will become nearly straight, and that the value of φ will be nearly equal to β. Thus, if the value of β is found by measuring the angles between the bands, the axis of the crystals arranged in the direction of the axis of the fibre will be known immediately.

Generally, taking a corner atom of the cubic lattice as the origin of a rectangular co-ordinate system and the edges of the cubic lattice as the axis of the co-ordinates, the angle β corresponding to an atomic plane with the indices h_1, h_2, h_3 will be given as follows:—

$$\cos\beta = \frac{h_1 l' + h_2 m' + h_3 n'}{\sqrt{h_1^2 + h_2^2 + h_3^2}} \quad \ldots\ldots\ldots\ldots(4)$$

where l', m', n': the direction cosines of the common axis of the crystals.

Now let us provisionally assume that the axis of the fibrous arrangement of the specimen coincides with a diagonal axis of the cubic lattice. Then the values of l', m' and n' will become

$$l' = 0 \qquad m' = n' = \frac{1}{\sqrt{2}} \quad \ldots\ldots\ldots\ldots(5)$$

and the expression (4) is reduced to

$$\cos\beta = \frac{h_2 + h_3}{\sqrt{2}\sqrt{h_1^2 + h_2^2 + h_3^2}} \quad \ldots\ldots\ldots\ldots(6)$$

From this equation, by assingning proper values to h_1, h_2, h_3 we obtain the values of β belonging to each atomic plane. The values thus obtained, are given in the left side of the Table 4.

On the other hand, the results of observations are given in the right side of Table 4, The values of β here given are obtained from Fig. 1,

1 Mem. Coll. Engineering, Kyushu, **2**, 247 (1922).

Table. 4.

Calculated Values		Observed Values		
Indices of Pls. h_1, h_2, h_3,	β	No. of Rad. Bds.	β	Indices of the Families of Pls.
1, 1, 0	0°	Ⅲ′	0°	(1, 1, 0)
3, 3, 1	13°13′	Ⅴ₀′	13°	(3, 3, 1)
0, 2, 1	18°23′	Ⅵ′	18°	(2, 1, 0)
1, 2, 1	30° 1′	Ⅶ′	30°	(2, 1, 1)
1, 1, 1 $\bar{1}$, 1, 1	35°16′	Ⅰ′	35°	(1, 1, 1)
0, 0, 1	45°	Ⅱ′	45°	(1, 0, 0)
3, 3, 1	49°32′	Ⅴ₀′ Ⅵ′	50°	(2, 1, 0)
1, 2, 0	50°56′			(3, 3, 1)
2, 1, 1	54°45′	Ⅶ′	54°	(2, 1, 1)
1, 1, 0 1, $\bar{1}$, 0	60°	Ⅲ′	60°	(1, 1, 0)
3, 3, $\bar{1}$	71° 4′	Ⅴ₀′ Ⅵ′	71°	(2, 1, 0)
2, 1, 0	71°34′			(3, 3, 1)
1, 2, 1	73°14′	Ⅶ′	73°	(2, 1, 1)
1, 0, 0				(1, 0, 0)
0, $\bar{1}$, 1	90°	Ⅰ′ Ⅱ′ Ⅲ′	90°	(1, 1, 0)
1, 1, 1				(1, 1, $\bar{1}$)

by measuring the inclination of each radiating band, and the indices of the atomic plane corresponding to it are taken from Table 3, which have previously been obtained from the position of the intense spots. As for the direction parallel to the axis of the fibrous arrangement in Fig. 1, from which the inclination of each radiating band is measured, we took the horizontal bands Ⅲ′ produced by the atomic plane (1, 1, 0).

Comparing the calculated and the observed values in Table 4. we observe that the agreement is fairly well within the limit of experimental errors. Next the writers tried to ascertain whether this result be also explainable by taking the prominent axes other than the diagonal of the crystal as the axis of the fibrous arrangement, but it was a failure. Accordingly it will not be unnatural to conclude that in the case of the standard figure the axis of the micro-crystals in the sample are arranged in a fibrous arrangement, and that the diagonal axes of the crystals are arranged in the direction of the axis of the fibre, which is parallel to the surface of the lamella.

As the consequence of our foregoing argument in connection with Fig. 8, Plate VI and Fig. 12, Plate VII, we may apply well the preceding

conclusion to the case when the fragment is not so large as in the case of Fig. 9, Plate VI. In such cases too, the arrangement of the micro-crystals in one of the mossy pieces will be the same as that of the standard figure. Fig. 9, obtained with a large foliated piece may easily be understood, if we consider that the foliated piece consists of many small lamellae of fibrous arrangement the axis of the fibre being distributed within the angular extension of each strip in the plane parallel to the surface of the lamella.

In short the arrangement of the micro-crystals in the specimen A may be summarized in the following two statements.

(1) Every piece of Specimen A consists of one lamella or several lamellae of fibrous arrangement, taking the diagonal axis of each cubic lattice as the axis of the fibre.

(2) When there exist a number of lamellae of fibrous arrangement in one piece of the specimen, the direction of the fibres are not strictly the same.

Next, to confirm the above consideration, the writers investigated the interference phenomena obtained in two orientations of the samples, one when it was rotated 22° around the direction parallel to the axis of the fibre, and the other when it was rotated 22° around an axis perpendicular to the axis of the fibre.

In both cases, the interference figures were photographed with the same large foliated fragment as was used in the case of Fig. 9, Plate VI. The distance between the photographic plate and the specimen was 3.5 cms. If our consideration be correct, the figure in the former case should remain unaltered; while in the latter case the symmetry of the figure should be violated. As was expected, the same interference figure Fig. 9, Plate VI, was obtained in the former case, but in the latter case the interference figure was quite different from the former one. Fig. 11, Plate VI is the photograph taken when the axis of the fibre was tilted from its vertical position toward the incident ray.

It is presumable that the same radiating bands as in Fig. 11 may be traced, if we find the relations between φ and θ, and between θ and r for a definite value of β corresponding to each atomic plane. To obtain the values of φ corresponding to values of θ from equation (3), the values of β given in Table 4 were employed, and for the values of α two values of $90^\circ - 22^\circ = 68^\circ$ and $90^\circ + 22^\circ = 112^\circ$ were taken. The values of φ corresponding to $\alpha = 68^\circ$, are given in the upper half of Table 5, and those corresponding to $\alpha = 112^\circ$, are given in the lower half of the same

table. The values of r corresponding to various of θ are calculated from equation (2) and they are given in Table 6. In Fig 2, the upper half corresponds to the case when $\alpha = 68°$, and the lower half corresponds to the case when $\alpha = 112°$.

Table. 5.
The Numerical Values of φ
(The Upper of Fig. 2)

θ \ β	0°	13°13′	18°23′	35°16′	45°	60°	90°
0°	—	—	—	28°17′	40°18′	57°22′	90°
3°	—	—	—	30°36′	42° 3′	58°45′	91°13′
5°	—	—	7°18′	31°57′	43° 6′	59°37′	92° 2′
10°	—	5°46′	14°32′	34°37′	45°18′	60° 5′	94° 5′
15°	—	11°49′	17°57′	36°32′	47° 3′	63°15′	96°13′
20°	—	14°	19°36′	37°48′	48°21′	64°44′	98°27′
30°	—	11°45′	18°29′	38°25′	49°39′	67° 5′	103°29′

(The Lower Half of Fig. 2)

θ \ β	0°	13°13′	18°23′	35°16′	45°	60°	90°
0°	—	—	—	28°17′	40°18′	57°22′	90°
3°	—	—	—	25°10′	38°17′	55°52′	88°47′
5°	—	—	—	23°10′	36°46′	54°47′	87°58′
10°	—	—	—	15° 7′	32°15′	51°46′	85°55
15°	—	—	—	—	26° 8′	48°19′	83°47′
20°	—	—	—	—	16°32′	46°52′	81°33′
30°	—	—	—	—	—	58° 8′	76°31′

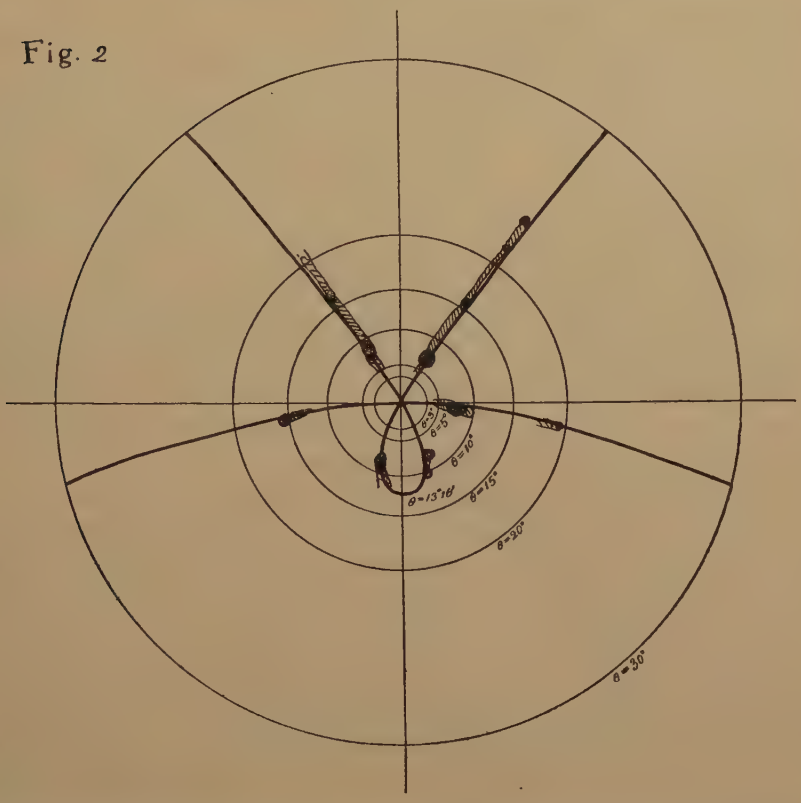
The part of the figure represented by the shadow in Fig. 2 is the copy of the figure of Fig. 11, Plate VI, while that represented by the thick full lines is the calculated lines corresponding to $\beta = 35°16'$ and $\beta = 90°$. These lines are caused by the reflection from the most prominent reflection plane (1,1,1), and they correspond to the strongest bands marked by I′ in the case of the normal incidence of the X-rays. As may be seen from the figure, the agreement between the calculated curves and the observed ones is satisfactory.

Table. 6.

θ	r
0°	0
3°	0, 3 7
5°	0, 6 2
10°	1, 2 7
15°	2, 0 2
20°	2, 9 4
30°	6, 0 6

(ii) Specimen B; This specimen can be classified in two parts, i. e., the main acicular part which has many long edges along its axis, and the granular part cosisting of many granules aggregated at the foot of the acicula.

Fig. 2



The Main Part:— By placing the axis of the acicular part parallel to the incident ray, we obtained the figure reproduced in Fig. 13, Plate VII. When the same axis was placed perpendicularly to the direction of the incident ray, so that the incident ray might sweep the periphery of the specimen the interference figure as shown in Fig. 14 Plate VII was obtained. In both cases, the photographic plates were set perpendicular to the incident beam in a position 3.2 cms, behind the specimen.

The prominent part of the figure reproduced in Fig.13, Plate VII consists of a set of Debye-Hull's rings associated with several Laue's spots. Though, the presence of Laue's spots shows that there are crystals of considerable dimensions, we may, however, from the predomination of Debye-Hull's rings, conclude that the majority of the micro-crystals in the specimen are irregularly orientated with respect to the direction of the incident ray.

Now, having confirmed that most of the micro-crystals in the specimen are irregularly orientated with respect to the direction of the incident ray,

only the following two cases are conceivable : —

(1) The case when the majority of the micro-crystals are irregularly orientated with respect to any direction.

(2) The case when the micro-crystals in the specimen are mostly so arranged that they have a definite common axis parallel to the acicular axis.

In order to decide which of these is the right one, let us consider the interference figure reproduced in Fig. 14.

In this figure, a set of radiating bands are predominant, which coincide well with the bands assigned by the same marks Ⅰ′ Ⅱ′, Ⅲ′ etc, in Fig. 1. Moreover, the intense spot on each radiating band of Fig. 14, comes out at the same position as that of Fig. 1. We may consequently conclude that the second case before mentioned applies well to the present arrangement. The fact that the interference figure in Fig. 14, Plate VII is essentially the same as the standard figure, indicates that the arrangement of the micro-crystals corresponding to the case of Fig. 14 should be the same as that corresponding to the standard figure, and that the micro-crystals in the acicular part should be mostly so arranged that the diagonal axis of each micro-crystal coincides with the acicular axis.

It can be expected from the above considerations that the acicular direction represented by ←→ in Fig. 14, should coincide with the direction of the axis of the fibrous arrangement, i. e., the direction of the radiating band Ⅲ′ belonging to the atomic plane 1, 1, 0. This expectation is also confirmed.

The consideration hitherto mentiond in connection with the acicular part lead us to the following conclusion:— The micro-crystals in the main acicular part of Specimen B are mostly so arranged, — similar to the case of Specimen A, — that the diagonal axis of each lattice coincides with the direction of the acicular axis, and that in other respects the orientation is at random.

In order to know whether the above conclusion may hold also good even in the inner region of the acicula, the writers experimeted with a specimen which was prepared by pickling the acicular part in dilute nitric acid. When the acicular part was pickled for a moderate time, it was disintegrated into several lamellae whose surfaces were parallel to the acicular direction. By transmiting the incident ray through a lamella placed normally to its direction, we obtained the figure reproduced in Fig. 10, Plate VI. This figure was essentially the same as that shown in Fig. 14, Plate VII.

Consequently, we know that the foregoing conclution in connection with the arrangement of micro-crystals in the periphery of the specimen holds also good even in the inner region of the specimen.

Granular Part: — The micro-structure of this part is shown in Fig. 7, Plate V. A number of twined crystals are vissible in this figure.

With a piece of this specimen, we obtained the figure which was reproduced in Fig. 15, Plate VII the distance between the specimen and the photographic plate being also 3.2 cms. in the present case. The prominent part of this figure consists of the complex mixture of Laus's spots, radiating bands, and Debye-Hull's rings.

From this figure, we may suppose that the most part of a granule consists of the irregular deposition of the micro-crystals, which contains several crystals of considerable size and of the fibrous arrangement. Furthermore, it may be natural to speculate that the fibrous pieces in this disposition are small fragments of the same constitution as those mentioned bofore.

From our foregoing argument in connection with Specimens A and B, we arrive at the following conclusions:—

(1) The silver micro-crystals have a tendency to deposit in the fibrous form.

(2) The diagonal axis of each cubic lattice is arranged in a direction parallel to the axis of the fibre.

The above conclusions contradict those of Glocker[1] and Bozorth[2], who endeavoured to suggest that electrolytically deposited silver has no regular orientation.

In conclusion, the writers wish to express their best thanks to Professor. M. Chikashige for his kind suggestions and interest, and to Professor. U. Yoshida for his kind guidance during the progress of experiment. Our thanks are also due to Mr. T. Miyoshi, by whose kind assistance some of the microscopic investigations were made.

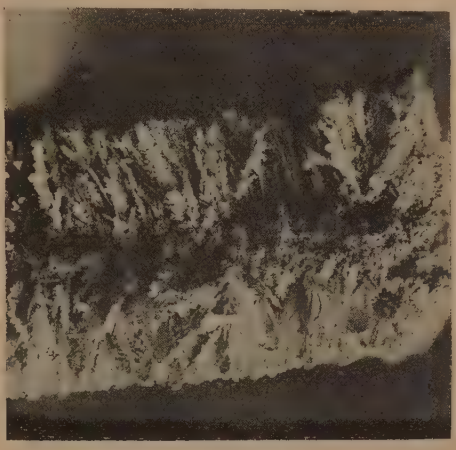
1 Loc. cit.

2 Loc. cit.

Fig. 3. Macro-structure of Specimen A
(view of transversal section)

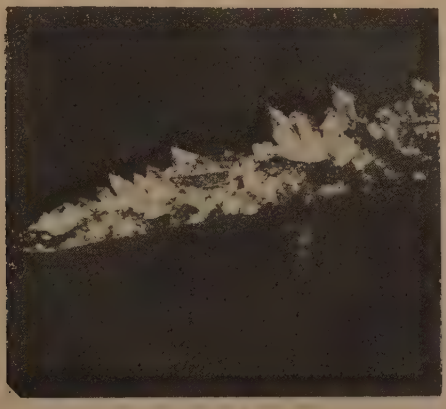
Size 1 : 1½

Fig. 4. Macro-structure of Specimen A
(view of longitudinal part)



Size 1 : 1½

Fig. 5. Macro-structure of Specimen B
(normal deposit)

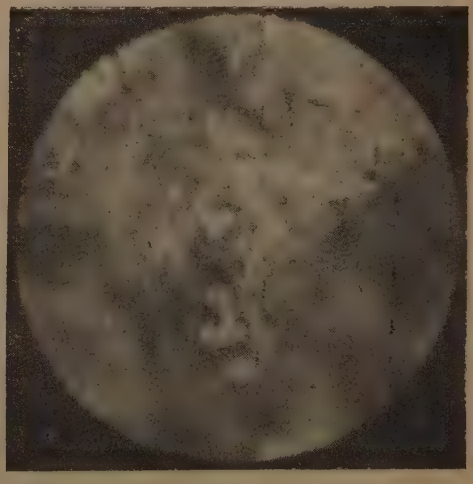


× 18

Fig. 6. Micro-structure of Specimen A
(mossy part)

× 200

Fig. 7. Micro-structure of Specimen B
(granular part)



× 140

Fig. 8. Specimen A

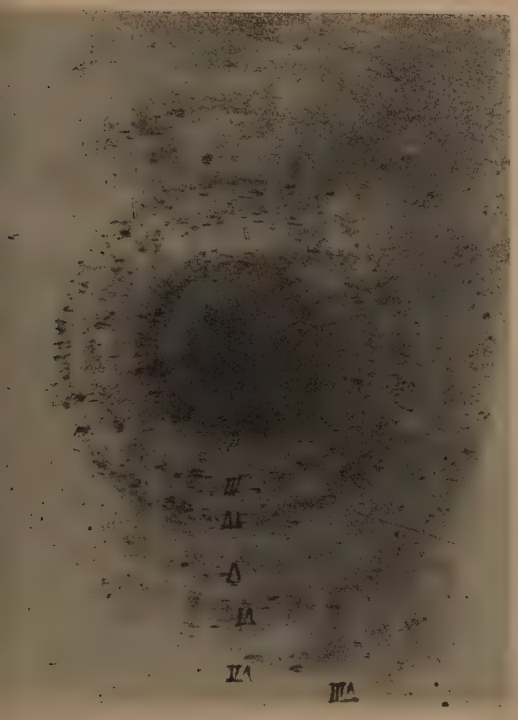


Fig. 9. Specimen A

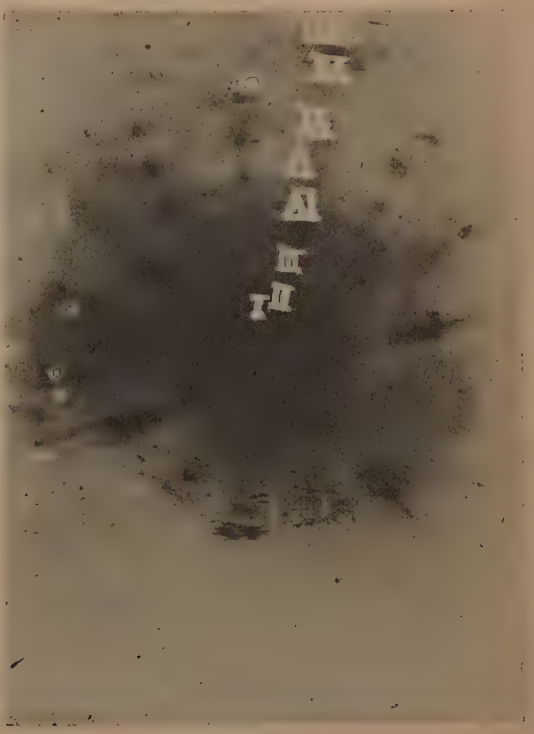


Fig. 10. Specimen B main part (inner)

Fig. 11. Specimen A

Transversal

Fig. 12 Specimen A

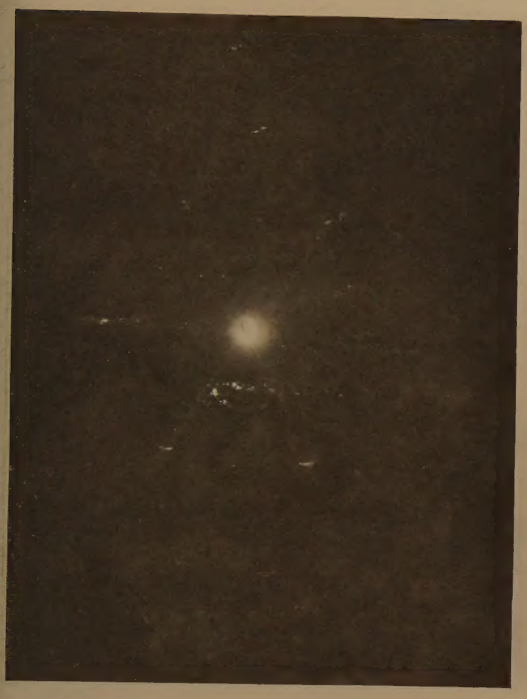
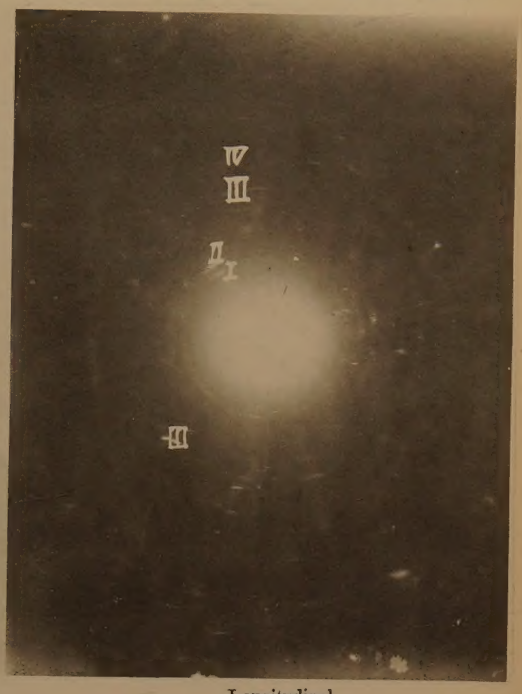
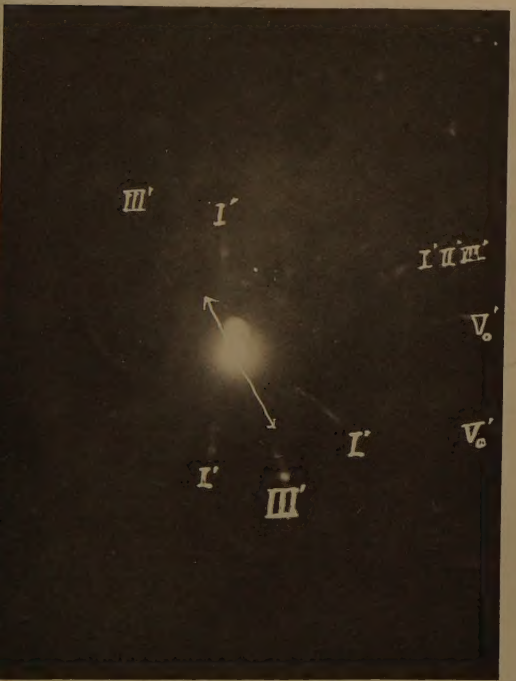


Fig. 13. Specimen B main part



Longitudinal

Fig. 14. Specimen B main part (periphery)



Transversal

Fig. 15. Specimen B granular part

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